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Improvement of Photoelectrochemical Hydrogen Generation by Surface Modification of p-Type Silicon Semiconductor Photocathodes

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Abstract: The improvement of H_2 evolution from two different types of catalytic p-type photocathode surfaces has been examined. p-Type Si has been platinized by photoelectrochemically plating Pt(0) onto the Si surface. Such a photocathode shows significant improvement (compared to naked p-type Si) for photochemical H_2 evolution with respect to output photovoltage, fill factor, and overall efficiency. Such photocathodes having an optimum amount of Pt(0) give a pH-dependent output voltage with respect to the H_2O/H_2 couple, but the dependence is not a simple 59-mV/pH dependence. No pH dependence would be expected if Pt(0) formed a Schottky barrier when plated onto p-type Si. A second kind of H_2 evolution catalyst has been confined to the surface of p-type Si. Polymeric quantities of an electroactive *N,N'*-dialkyl-4,4'-bipyridinium reagent, $(PQ^{2+/+\cdot})_n$, have been confined to the surface. The Br^- counterions of the polymer are then exchanged by $PtCl_6^{2-}$. Photoreduction then yields Pt(0) dispersed in the polymer. Such a surface is again significantly improved compared to naked p-type Si with respect to H_2 evolution. A comparison of the naked p-Si, the simply platinized, and the $[(PQ^{2+/+\cdot})_n \cdot n\mathrm{Pt}(0)]_{\mathrm{surf.}}$ system is made and contrasted to the expected behavior of an external Schottky barrier photocell driving an electrolysis cell with a Pt cathode. Experiments with n-type MoS_2, n-type Si, Pt, Au, and W cathodes functionalized with the $[(PQ^{2+/+\cdot})_n \cdot n\mathrm{Pt}(0)]_{\mathrm{surf.}}$ system compared to the same surfaces directly platinized confirm an important difference in the mechanism of H_2 evolution catalysis for the two surface catalyst systems. For the $[(PQ^{2+/+\cdot})_n \cdot n\mathrm{Pt}(0)]_{\mathrm{surf.}}$ system there is an optimum pH for the catalysis, consistent with the pH-independent formal potential of the $(PQ^{2+/+\cdot})_n$ system, -0.55 ± 0.05 V vs. SCE, relative to the formal potential of the (H_2O/H_2) couple that moves 59 mV per pH unit. Qualitative experiments with insulating glass surfaces derivatized with $[(PQ^{2+/+\cdot})_n]_{\mathrm{surf.}}$ establish directly that the Pt(0) is necessary, and sufficient, to equilibrate $(PQ^{2+/+\cdot})_n$ with (H_2O/H_2). p-Type Si modified with optimum amounts of Pt(0) by direct platinization appears to give improved H_2 evolution efficiency by a mechanism where the Pt(0) serves as a catalyst that does not alter the interface energetics of the semiconductor.

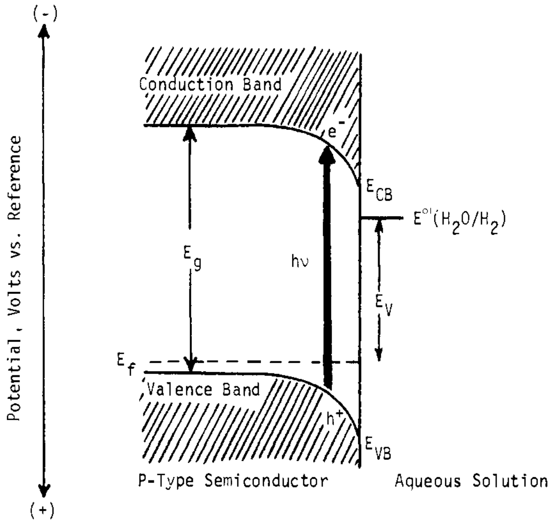
Small band-gap, p-type semiconducting photocathode materials are now recognized to have rather poor surfaces from which to evolve H_2.[1-7] This is unfortunate since it would appear that small band-gap p-type semiconductors contacting liquid electrolyte solutions do not undergo rapid corrosion reactions despite their thermodynamic instability.[8] We and others have previously illustrated ways to improve the overall efficiency for H_2 evolution.[1-7,9]

With reference to Scheme I, the problem can be simply stated: the H_2 generation is often energetically feasible (E_{CB} more negative than $E°'(H_2O/H_2)$), but the rate of H_2 generation does not compete with e^-–h^+ recombination at a small band bending where both a reasonable output photovoltage, E_V, and a reasonable photocurrent could, in principle, be realized.[7] Thus, efficiency improvement hinges on being able to accelerate the *rate* of H_2 evolution from the surface. Otherwise, the photocathode potential, E_f, must be held so negative compared to $E°'(H_2O/H_2)$ that E_V is small.

We take efficiency, η, to be given according to eq 1

$$\eta = \frac{E_V i}{\text{Optical Power In}} \times 100\% \tag{1}$$

Scheme I. Interface Energetics for a p-Type Semiconductor Contacting an Aqueous Electrolyte Where the Excited Electron, e^-, Is Thermodynamically Capable of Reducing H_2O with a Photovoltage of $>E_V$ [a]



[a] Generally, the H_2 generation rate is low at large values of E_V, since e^--h^+ recombination can compete with the H_2 generation when band bending is relatively small. In this and subsequent schemes, E_{CB} and E_{VB} are the bottom of the conduction band and the top of the valence band at the interface, respectively. E_f is the electrochemical potential of the semiconductor, and E_g is the band gap of the semiconductor.

where $E_V \equiv$ photovoltage in volts, $i \equiv$ photocurrent in amps, and the Optical Power In is in watts. The E_V is the extent to which the electrode potential, E_f, is more positive than the formal potential, the H^+/H_2 couple, $E°'(H^+/H_2)$, when there is photocurrent, *i*. The η is a measure of the extent to which the input optical power is transduced to the power needed to reduce H_2O. When either E_V or *i* is zero, the value of η is zero. The objective

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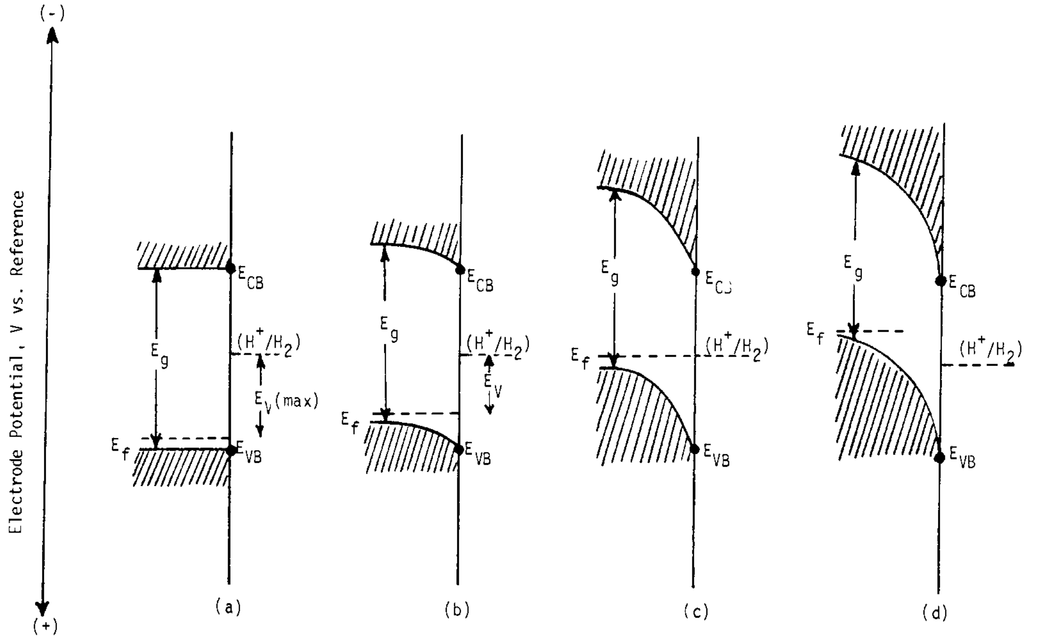
Scheme II. Representation of the Effect of Varying Electrode Potential, E_f, on the Interface. Energetics for a p-Type Semiconductor Contacting an Aqueous Electrolyte Solution



[a] In (a) $E_f = E_{FB}$ and the difference in E_f and (H^+/H_2) is the maximum attainable photovoltage, E_V(max), and is also the maximum amount of band bending that can occur at $E_f = (H^+/H_2)$. In (b) there is a small amount of band bending so that photogenerated carriers can be separated to give a photocurrent. Such a situation corresponds closely to what would be called the maximum power point where E_V is good and the band bending is sufficient to separate the charge carriers. For H_2 evolution the kinetics for H_2 formation are too sluggish to compete with recombination of the e^--h^+ pairs. In (c) $E_f = (H^+/H_2)$ and the value of E_V is zero. In (d) photocurrent for H_2 generation would not represent conversion of light to chemical energy, since E_f is more negative than (H^+/H_2). This means that the formation of H_2 is thermodynamically spontaneous in the absence of light. The role of light would simply be to generate the minority carrier needed to effect the cathodic process.

is to optimize the value of E_Vi. When E_Vi is its maximum value, the associated value of E_f is the so-called maximum power point. At open circuit and at high light intensity, the bands of the semiconductor flatten as E_f moves more positive; at open circuit E_V thus reaches its maximum value, E_V(max), but η is zero at the associated E_f since no current can flow at open circuit. The objective is to minimize the loss in E_V required to achieve good H_2 generation rate. Hence, we focus on the improvement of H_2 evolution kinetics in this paper.

The representation of the p-type semiconductor/electrolyte interface in Scheme I does not adequately illustrate all of the important aspects of such interfaces. In particular, it should be noted that for the small band-gap semiconductors Si (E_g = 1.1 eV),[1,4] GaAs (E_g = 1.4 eV),[10] and InP (E_g = 1.3 eV),[6] the positions E_{CB} and E_{VB} do not remain fixed as $E^{\circ\prime}$ is varied.[11] In fact, for a considerable fraction of the potential range of the formal potential $E^{\circ\prime}(H_2O/H_2)$, -0.24 V vs. SCE at pH 0 to -1.1 V vs. SCE at pH 14, variation in $E^{\circ\prime}$ does not result in a significant change in E_V(max) as might be expected.[11] This phenomenon may be due to interface states[11] or to carrier inversion[12] or to a combination of these.

Scheme II gives a representation of effects of E_f variation starting at $E_f = E_{FB}$, the so-called flat-band potential of the semiconductor. This diagram aids in understanding the photocurrent voltage (i vs. E_f) curves associated with a photocathode. As E_f moves more negative, there is a significant amount of band bending such that the photogenerated minority carrier is driven to the interface to come to a potential E_{CB}. But at some point $E_f \equiv E^{\circ\prime}(H_2O/H_2)$, a more negative shift in E_f does not allow any output voltage. When E_f is more negative than $E^{\circ\prime}(H_2O/H_2)$, reduction to form H_2 is thermodynamically possible in the dark, and light serves only to create carriers.

With respect to H_2O reduction, the point is that for a given semiconductor E_V(max) is attainable, in principle, but the kinetics for reduction of H_2O are so poor that little or no current for H_2O reduction occurs until E_f is more negative than $E^{\circ\prime}(H_2O/H_2)$. In practical terms this means that the light plays no role beyond creation of the reducing equivalent. The light does not contribute to the power necessary to reduce H_2O. In fact, a cathode having low H_2 overvoltage that does not require illumination to create the reducing equivalents is better from the standpoint of energy conversion. For the conventional electrode only electricity is needed to reduce H_2O; for the photocathodes just as much electrical energy (or even more) is needed, but in addition, light is required.

We were stimulated to attempt to catalyze the evolution of H_2 from photocathodes after we and others[1-7] demonstrated that the oxidized form of certain redox couples could be very efficiently photoreduced at p-type semiconductor photocathodes. In particular, redox materials such as *N,N'*-dimethyl-4,4'-bipyridinium, MV^{2+}, where $E^{\circ\prime}(MV^{2+/+\cdot}) \approx E^{\circ\prime}(H_2O/H_2)^4$ at pH ~7, can be efficiently photoreduced under conditions where H_2O is not. In fact, comparisons such as MV^{2+} reduction vs. H_2O reduction establish[1-7] that kinetics, and not energetics, are the impediment to high efficiency for H_2 generation at p-type semiconductor photocathodes.

The amount of band bending when $E_f = E^{\circ\prime}(H_2O/H_2)$ may be the value of E_V(max). As indicated above, the band bending could be fixed for an important range of potentials. In some instances the fixed value of band bending may be due to interface states.[11] Accordingly, we have focused on surface modification as a technique to change the kinetics for H_2O reduction. Surface modification could change the interface states and alter energetics as well.[4,11] For the range of potentials where the band bending is the same, we refer to the system as being Fermi level pinned,[11] and often it appears that the same band bending is obtained for a semiconductor/metal (Schottky barrier) interface.[13] We thus

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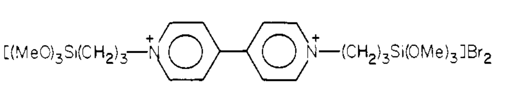
compare the results from our surface modification procedures for catalysis to the expected properties of a Schottky barrier cell driving an electrolysis cell where the cathode is a good H_2 electrode such as Pt.

In this article we wish to present results on the photoelectrochemical behavior of three kinds of H_2 evolution systems based on light absorption by p-type Si: (i) "naked" (etched, but not otherwise deliberately modified) p-type Si; (ii) p-type Si onto which Pt(0) has been electrochemically deposited;[9] and (iii) p-type Si first derivatized with reagent I to yield an electroactive, surface-confined polymer into which Pt(0) is then dispersed.[7,14,15] In particular, we have determined the pH dependence of the photoelectrochemical generation of H_2 and have studied the mechanism of the catalysis of H_2 evolution on the modified surfaces. Modified Au, Pt, W, n-type Si, and n-type MoS_2 electrodes have been examined to evaluate certain features of the H_2 evolution catalysts.



I

Experimental Section

General Procedure. Cyclic voltammetry and steady-state current-voltage data were obtained using a PAR Model 173 potentiostat equipped with a Model 179 digital coulometer and a Model 175 voltage programmer. All data were recorded on a Houston Instruments X-Y recorder. Experiments were performed in a single-compartment Pyrex cell with a saturated calomel reference electrode (SCE), Pt counterelectrode, and the appropriate working electrode. Photoelectrodes were illuminated using a beam-expanded 632.8-nm He-Ne laser (Coherent Radiation) providing up to ~50 mW/cm^2 over the entire electrode surface. Buffer solutions were 1.0 M KCl solutions from distilled deionized H_2O buffered as follows: pH 8.0, 0.05 M $(CH_2OH)_3CNH_2$ + 0.029 M HCl; pH 7.0, 0.05 M KH_2PO_4 + 0.029 M NaOH; pH 6.0, 0.05 M KH_2PO_4 + 0.0056 M NaOH; pH 5.0, 0.1 M $NaCH_3COO$ + 0.05 M CH_3COOH; pH 4.0, 0.1 M $NaCH_3COO$ + 0.4 M CH_3COOH; pH 3.0, 0.05 M $KH(C_8H_4O_4)$. pH 2.0 or 1.0 was established by the presence of 0.01 M HCl or 0.1 M HCl, respectively. Actual solution pH was measured using a Corning pH Meter. The $Ru(NH_3)_6Cl_3$ was obtained from Alfa-Ventron and used as received.

Electrodes. Single-crystal, B-doped, p-type Si wafers (0.25 mm thick, (111) face exposed, resistivity of 3-7 ohm-cm) were obtained from Monsanto Co. Ohmic contacting and mounting procedures are as previously described.[1,4,7,14] Single-crystal, P-doped, n-type Si (Monsanto, (111) face exposed, 3-7 ohm-cm) is that used and previously characterized.[16] Pt and Au electrodes were made from small sheets (4 mm × 8 mm) of the respective metals. W electrodes consisted of a length of W wire (0.030 in. diameter) insulated with heat shrink tubing leaving a 1.4-cm length exposed as the working electrode surface. n-Type MoS_2 is that used and previously characterized.[17] p-Type Si is contacted by first evaporation of Al onto the Si pretreated by etching in concentrated HF for 60 s. The Al/Si is then annealed at 450 °C for 5 min under N_2. The copper wire lead is then attached with conducting Ag epoxy.

Rotating Disk Electrodes.[18] Rotating disk electrodes were fashioned by cutting 4-mm circles of the appropriate electrode materials (Pt, Au, n- or p-Si). The metals were contacted with Ag epoxy and the semiconductors were first ohmically contacted as previously and then contacted with Ag epoxy. These electrodes were sealed onto the flattened end of 5-mm o.d. glass capillary tubing, and the exposed edges were sealed with ordinary epoxy to define an electrode with an exposed, projected surface ~3 mm in diameter. Electrical contact to the Ag epoxy on the back side exposed to the capillary was established using liquid Hg, and a Cu wire was inserted into the Hg liquid. The finished electrodes were mounted in the shaft of a variable-speed stirring motor from Polysciences, Inc. Speeds from 200 to 2400 rpm can be obtained. The actual speed was established by calibrating the motor settings with a photodiode connected to a tachometer (Power Instruments, Inc., Skokie, Ill.). These readings were also checked by monitoring the response of a photodiode to an irradiated reflector mounted concentrically on the disk shaft using a calibrated oscilloscope to measure the photodiode output. The Pt and Au rotating disk electrodes were checked by monitoring the current, i, vs. $\omega^{1/2}$ (rotation velocity)$^{1/2}$, at +0.7 V vs. SCE for the oxidation of 4 mM $Fe(CN)_6^{4-}$ in 2 M KCl. n-Type Si disks were tested under illumination (632.8 nm, ~5 mW) at +0.5 V vs. SCE in EtOH/0.1 M $(n\text{-}Bu_4N)ClO_4$ containing 4 mM $Fe(\eta^5\text{-}C_5H_5)_2$. p-Type Si disks were tested under illumination (632.8 nm, 5 mW) at -0.5 V vs. SCE in 1.0 M KCl (aqueous) containing 2 mM $Ru(NH_3)_6^{3+}$. The test redox couples $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$, and $Fe(\eta^5\text{-}C_5H_5)_2^{+/0}$ were chosen for convenience and their fast heterogeneous electron-transfer kinetics. Plots of i vs. $\omega^{1/2}$ are linear up to the highest rotation velocity (at 2400 rpm) for acceptable electrodes.

Synthesis of I. Synthesis and characterization of I are as follows.[14] Dry 4,4'-bipyridine (1.0 g, 0.67 mmol) (Aldrich) in dry CH_3CN (600 ml) was added to 1-bromo-3-trimethoxysilylpropane (II) (12.5 g, 0.05 mol) [prepared by reacting 4 equiv of $HC(OMe)_3$ with 1-bromo-3-trichlorosilylpropane (Petrach Co.), then fractionally distilling II (bp 85 °C (10 mm Hg))]. The mixture was refluxed for 14 days, cooled to 298 K, and filtered to collect I. The product I was then recrystallized twice from CH_3CN/Et_2O and isolated as a solid pale-yellow bromide salt, yield 90%. Compound I readily dissolves in D_2O (accompanied by hydrolysis) to give the following ^1H NMR (δ, D_2O, 90 MHz): 0.84 (4 H, m), 2.24 (4 H, m), 3.37 (18 H, s), 4.78 (4 H, t, J = 7 Hz), 8.61 (4 H, d, J = 7 Hz), 9.17 (4 H, d, J = 7 Hz). Prominent IR absorptions for I in a KBr pellet are at 1637 (m), 1385 (vs), 1196 (m), and 1080 (s) cm^{-1}. The electronic absorption spectrum of I shows a strong band at 255 nm ($\epsilon \approx 25000$ M^{-1} cm^{-1}) in CH_3CN. Anal. (Schwartzkopf) [calcd (found)]: C, 41.13 (40.63); H, 5.96 (5.81); N, 4.36 (4.23); Si, 8.74 (8.76); Br, 24.87 (24.68).

Surface Attachment of I. Surface pretreatment of n- and p-type Si,[4,7,14,19] Pt,[20,21] and Au[20] for functionalization with I was as outlined previously. The W pretreatment consisted of immersing the wire in concentrated HNO_3 for ~2 min followed by rinsing with distilled H_2O and drying. n-Type MoS_2 was functionalized after washing with concentrated HCl. After the appropriate pretreatment, derivatization with I is effected by immersing the electrode material in a CH_3CN solution containing 1-3 mM I for 3-24 h, followed by rinsing with CH_3CN and then acetone. Such solutions are not rigorously free of H_2O; the trace H_2O allows hydrolysis of I to promote attachment of polymers based on I; cf. Scheme IV. For Pt, Au, W, and n-MoS_2, derivatization with I was also effected by potentiostatting the pretreated electrode at -0.7 V vs. SCE in aqueous 0.2 M KCl and 0.1 M K_2HPO_4 (pH 8.9), solution of ~3 mM I. The solution was not stirred and the derivatization was carried out under N_2 or Ar for 3 to 4 h. Coverage of the polymer, $(PQ^{2+})_n$, from I was determined by integration of cyclic voltammetry waves for $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$.

Incorporation of Pt(0) into the $(PQ^{2+/+\cdot})_n$ Polymer. Incorporation of the Pt(0) catalyst into the polymer of I was accomplished by dipping the electrode into an aqueous solution of 1 mM $PtCl_6^{2-}$ (dihydrogen or dipotassium salt) for ~30 s at 298 K.[7] The electrode was then rinsed with distilled water. Reduction of Pt(IV) → Pt(0) within the polymer was effected by immersing the potentiostated electrode into the electrolyte solution at -0.6 V vs. SCE, and with ~50 mW/cm^2 illumination at -0.3 V vs. SCE for the p-Si photocathodes.

Surface Platinization. Prior to platinization, the p-type Si electrode was etched in concentrated HF for 30 s and characterized by its photocurrent voltage properties in a pH 7 phosphate buffer using 632.8-nm illumination at ~50 mW/cm^2. After re-etching for 30 s in concentrated HF, the electrode was potentiostated at -0.3 V vs. SCE (in some cases -0.6 V) in the platinizing solution and irradiated at 632.8 nm, 50 mW/cm^2. For W or n-type Si, platinization is accomplished by potentiostating at -0.1 V vs. SCE in the platinizing solution. The platinizing solution consisted of a 0.1 M $NaClO_4$, ~1 × 10^{-3} M K_2PtCl_6 aqueous solution.

The quantity of Pt(0) deposited electrochemically was followed using a digital coulometer. Initial platinization of p-type Si typically involved

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Table I. Representative Efficiencies for Conversion of 632.8-nm Light to Chemical Energy Using Platinized p-Type Si-Based Photoelectrochemical Cells

platinized p-Si electrode[a]	electrolyte soln	$E°'(H_2O/H_2)$, V vs. SCE	input, mW/cm²[b]	Φ_e at $E°'(H_2O/H_2)$[c]	E_V(max), mV[d] (E_V at η_{max}, mV)	η_{max}, %[e]
1	H_2O, pH 6.6	−0.63	6.4	0.63	400 (200)	5.4
	pH 5.3	−0.55	6.4	0.63	380 (200)	5.0
	pH 4.0	−0.48	6.4	0.63	360 (180)	4.7
	pH 1.3	−0.32	6.4	0.63	260 (120)	2.7
2	H_2O, pH 5.4	−0.56	11.8	0.83	460 (220)	7.1
	pH 3.9	−0.47	11.8	0.83	400 (190)	6.9
	pH 1.1	−0.31	11.8	0.83	260 (120)	3.5
3	H_2O, pH 6.5	−0.62	11.8	0.72	320 (160)	4.1
	pH 3.9	−0.47	11.8	0.72	320 (110)	2.3
	pH 1.1	−0.31	11.8	0.72	140 (30)	0.4

[a] Platinized p-Si electrodes were prepared by electroplating Pt onto the surface; see Experimental Section. [b] Input is at 632.8 nm. [c] Quantum yield for electron flow measured at $E°'(H_2O/H_2)$. [d] Output photovoltage, E_V, is the extent to which photocathodic current can be observed at a more positive potential than $E°'(H_2O/H_2)$; see Scheme I in text. [e] Efficiency; see eq 1 in text.

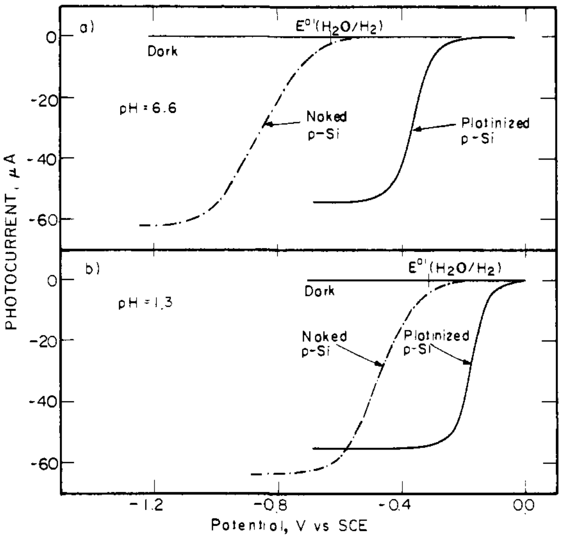

Figure 1. Steady-state photocurrent–voltage curves for naked p-type Si (–•–•) and for platinized p-Si (—). (a) Aqueous solution buffered to pH 6.6; (b) aqueous solution at pH 1.3 with $HClO_4$. Illumination is at 632.8 nm, ~2.5 mW/cm². See Table I for energy conversion efficiency. The platinized p-type Si was prepared by photoelectrochemical reduction from 1×10^{-3} M K_2PtCl_6 in 0.1 M $NaClO_4/H_2O$ at −0.3 V vs. SCE until 1.1×10^{-2} C/cm² had passed.

passing $\sim 3 \times 10^{-2}$ C/cm² of cathodic charge. The electrode was then rinsed with distilled H_2O and again checked for its photocurrent–voltage properties in pH 7 buffer. If necessary, further platinization was carried out as described to a total of no more than 10^{-1} C/cm². For W or n-type Si electrodes, platinization of $\sim 2 \times 10^{-2}$ C/cm² was used. These values for the quantity of Pt(0) deposited are approximate for two reasons: (i) dipping the electrodes into the solution without passing charge results in some Pt(0) deposition, and (ii) when Pt(0) is deposited in amounts near optimum, H_2 evolution begins to account for a small fraction of the cathodic current.

Auger Spectroscopy and Depth Profile Analysis. Auger spectra and depth profiles were obtained using a Physical Electronics Model 590A scanning Auger spectrometer. A 5-keV electron beam with a beam current from 0.3 to 2 μA was used as the excitation source. Depth profiling using an Auger spectrometer has been previously described.[22] A Physical Electronics Model 04-303 differential ion gun was used to produce a 2-keV Ar^+ ion beam for sputtering. The pressure was maintained at $\sim 3 \times 10^{-7}$ Torr in the main vacuum chamber, and 1.5×10^{-4} Torr of Ar in the ionization chamber. Si samples were mounted by attaching the Cu wire lead to the sample holder, and Pt, Au, or W samples were clipped down to ensure electrical grounding. Generally, signals for C, N, O, Si, Pt, the counterion of $(PQ^{2+})_n$, and the substrate were analyzed as a function of sputtering time. The energy window used was typically 10–50 eV around the energy characteristic of the element being analyzed. No interferences from other elements were encountered when using the following characteristic Auger signals (in eV):[23] C (272), N (379), O (503), Si (1619), Pt (1967), Au (2024), W (1736), and Br (1396). The Cl (181 eV) signal encountered interference from W signals, and to a lesser extent from Au and Pt signals. With our spectrometer only six elements can be monitored during depth profiling. All elements characteristic of the surface polymer and the substrates have been examined in the course of these studies and all data are consistent with a $(PQ^{2+})_n$ system that is constant in composition from electrode to electrode and through its entire thickness (except for the outermost layer) to the limits of resolution of the profiling technique.

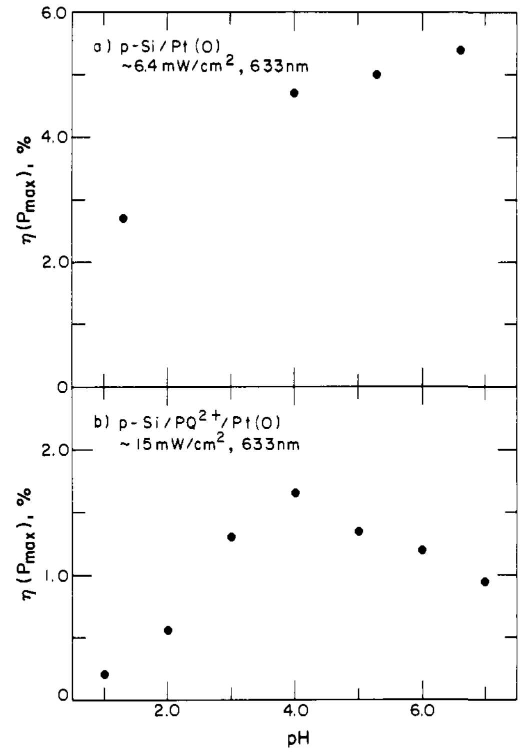

Figure 2. Efficiency (see eq 1 of text) for H_2 generation from (a) platinized p-type Si and (b) p-type Si modified with $[(PQ^{2+})_n \cdot nPt(0)]_{surf.}$ (PQ^{2+} coverage = 2×10^{-8} mol/cm²) as a function of pH. The 633-nm illumination intensity is as shown. Electrode areas are ~0.1 cm². Data in (a) are for electrode 1 of Table I, and data in (b) are for electrode 4 of Table III.

Results

a. Platinized p-Type Si vs. Naked p-Type Si Photocathodes for H_2 Generation. Figure 1 shows a comparison of the photocurrent–voltage curves associated with platinized and naked p-type Si photocathodes at two different pH's. The qualitative effect from platinizing found here is like that previously reported for

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(22) (a) Palmberg, P. W. *J. Vac. Sci. Technol.* **1972**, *9*, 160. (b) Holloway, D. M. *Ibid.* **1975**, *12*, 392.

(23) Davis, L. E.; MacDonald, N. C.; Palmberg, P. W.; Riach, G. E.; Weber, R. G. "Handbook of Auger Electron Spectroscopy", 2nd ed.; Physical Electronics Division, Perkin-Elmer Corp.: Eden Prarie, Minn., 1972.

a single pH value.[9] Naked p-type Si shows little, if any, photocurrent at potentials significantly positive of $E^{\circ\prime}(H_2O/H_2)$ whereas the platinized electrode surface shows a photocurrent onset ~500 mV more positive than $E^{\circ\prime}(H_2O/H_2)$; i.e., $E_V \approx 0.5$ V (cf. Scheme I). Data culled from curves such as those given in Figure 1 are collected in Table I for a number of independently prepared photocathode surfaces. The main finding, of course, is that the platinizing procedure significantly improves the efficiency for the photoelectrochemical generation of H_2 compared to naked p-type Si. Our new data also show that the improvement that can be realized depends on the pH such that the low pH's give lower efficiency. Figure 2 shows a typical profile of efficiency vs. pH.

Data in Figure 1 and Table I are for electrodes that bear what we found to be the optimum amount of Pt(0) when checked at pH ~7. By optimum amount we mean the amount that is sufficient to give the highest efficiency and not so much that the incident light is attenuated by the Pt(0) on the surface. Very low Pt(0) coverage gives photocurrent–voltage curves that are intermediate between those for the naked p-type Si and those as in Figure 1 for platinized p-type Si. But even very low Pt(0) gives an onset for H_2 evolution as positive as when Pt(0) is at optimum coverage. The low Pt(0) coverages give poor fill factors. Generally, we find that a coverage of $\sim 5 \times 10^{-8}$ mol of Pt/cm^2 is optimum. But this number is not accurate since the Pt(0) is plated on in H_2O solution and once some Pt(0) is deposited H_2 evolution commences at the pH and potential used in the platinization. Another complication is that some improvement for H_2 evolution is achieved by simply immersing the p-type Si into $PtCl_6^{2-}$ solution. The photocurrent–voltage curves from simple immersion are intermediate between those for naked and optimum amounts of Pt(0). The improvement in H_2 evolution performance from only dipping the electrode into $PtCl_6^{2-}$ is a short-lived phenomenon and does not even allow the recording of reproducible steady-state photocurrent–voltage curves; less than 2 min of constant photocurrent is obtained whereas optimally platinized samples give constant photocurrent for <1 h.

A good procedure for platinization has been to photoelectrochemically plate Pt(0) from $PtCl_6^{2-}$ until the optimum photoelectrochemical performance is achieved. Efficiencies given according to eq 1 in the vicinity of 5–6% are routinely possible with our platinized samples, whereas naked p-type Si gives <<1% at any pH studied. The durability of the platinized photocathodes is certainly sufficient to run the number of steady-state photocurrent–voltage curves that allows conclusions to be drawn concerning the pH effects. We have, for example, run steady-state photocurrent–voltage curves from 0.0 to –0.6 V vs. SCE at a rate of 10 mV/s at three different pH's. Returning to the original pH shows the same results as the initial run. However, the efficiency deteriorates over a period of several hours when operating at the maximum power point. We have not optimized conditions for plating the Pt for purposes of long life, and at this time we are not certain of the reason(s) for the deterioration with time.

The finding of importance with respect to the mechanism of improving the H_2 evolution efficiency is that the efficiency depends on pH. A priori, it would seem that plating Pt onto the surface of p-type Si would yield a semiconductor/oxide/metal interface system whose photovoltaic properties would be independent of pH, since the photovoltaic junction is "buried" and the Pt metal contacts the aqueous solution. A semiconductor/oxide/metal photovoltaic electrode would seemingly be equivalent to a photovoltaic (Schottky) device in series in the *external* circuit of an electrochemical cell where the cathode of the cell is Pt. The efficiency from the photovoltaic would be independent of pH provided the kinetics at the electrodes were independent of pH. Poor kinetics would lower the efficiency since this leads to larger voltage requirements. Thus, poor kinetics for H_2 evolution at low pH could account for the efficiency vs. pH profile, but the notion that H_2 kinetics are worse in acid vs. neutral solution is not consistent with what is known about H_2 evolution from Pt.[24] However, Pt on Si may behave differently.

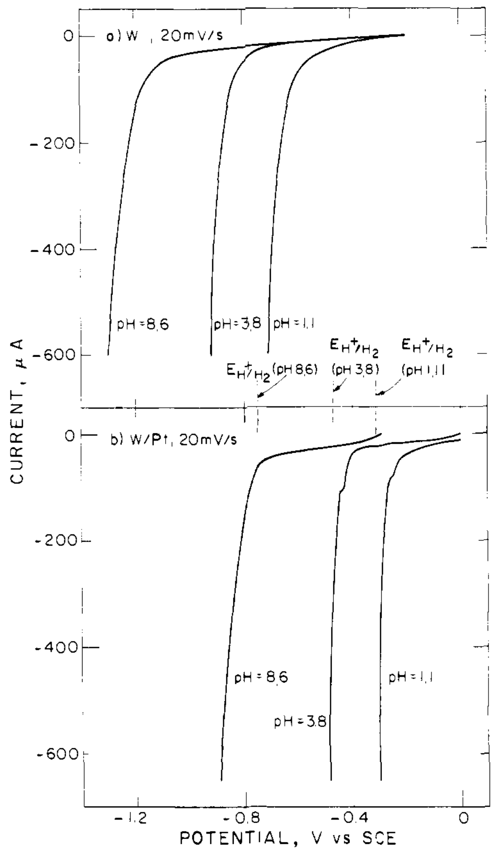

Figure 3. Steady-state current–voltage curves for (a) W wire and (b) platinized W (4.0×10^{-8} mol/cm^2) in aqueous pH buffer solutions (left to right) of 8.6, 3.8, and 1.1. Potential was swept at a scan rate of 20 mV/s.

An alternative explanation for the low efficiency at low pH's is that the Pt coverage is non-uniform and that the semiconductor/oxide contacts the aqueous electrolyte to an extent that the interface energetics, i.e., E_{CB}, E_{VB} positions, are dependent on the solution. In the acid solutions the value of E_V is lower than in neutral solution in a manner consistent with the fact that $E^{\circ\prime}(H_2O/H_2)$ is more positive and in a potential range where E_V is dependent on the electrochemical potential of the solution.[4,25]

Whatever the mechanism, the platinized p-type Si does not behave as a "buried" photovoltaic junction. Experimentally it is not equivalent to a photovoltaic in series with an electrolysis cell employing a Pt cathode. In the next section we describe the results which show that the kinetics for H_2 from deposited Pt can be quite good. This leads to the conclusion that the deposited Pt incompletely covers p-type Si leading to a photoelectrode whose properties are dominated by contact of the electrolyte solution, not the Pt, with the Si/SiO_x surface.

b. Current-Voltage Properties of Platinized n-Type Si and Platinized W Electrodes. n-Type Si[4] and W electrodes are poor electrodes for H_2 evolution. Figure 3 shows the current–voltage curves for W cathodes for H_2 evolution as a function of pH before and after platinization. The amount of Pt(0) deposited is as close as possible to that used to give optimum properties for platinized p-type Si photocathodes. The platinization of W gives an obvious improvement for H_2 evolution. The onset of current is very close to that expected on thermodynamic grounds at each of the pH's, and a high current density, >10 mA/cm^2, is achievable with a cathode potential no more than 100 mV more negative than $E^{\circ\prime}(H_2O/H_2)$. The current–voltage properties are somewhat better at the lower pH's. These results parallel expectation and suggest that deposited Pt can yield electrodes having sufficiently good H_2 kinetics to ensure that the efficiency of platinized pho-

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(24) Frumkin, A. N. *Adv. Electrochem. Electrochem. Eng.* **1964**, *3*, 287.

(25) Heller, A.; Lewerenz, H. J.; Miller, B. *J. Am. Chem. Soc.* **1981**, *103*, 200.

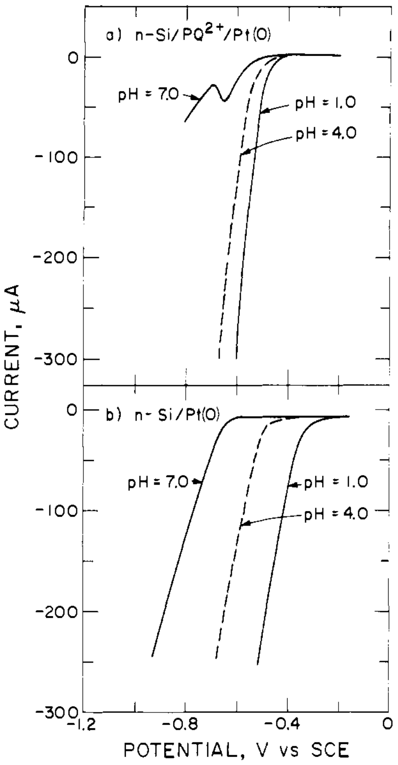

Figure 4. Steady-state (10 mV/s) current–voltage curves for n-type Si (~0.1 cm^2) derivatized with (a) $[(PQ^{2+})_n{\cdot}nPt(0)]_{surf}$ (PQ^{2+} coverage of ~2 × 10^{-8} mol/cm^2) and (b) with only Pt(0) as a function of pH. The small peak at pH 7.0 in (a) corresponds to $(PQ^{2+})_n \rightarrow (PQ^{+\cdot})_n$. The steady-state cathodic current is due to H_2 evolution.

tocathodes should not be limited by this parameter.

The results for W are equivocal in one respect in that the deposition of Pt(0) onto various materials may not lead to the same results, especially at the low levels of Pt(0) deposited. It is well known that there is considerable difficulty in electrochemically depositing continuous metal films when small amounts of metal are deposited. Accordingly, we have examined the behavior of platinized n-type Si. Unlike p-type Si, n-type Si is not blocking to reductions in the dark. Generally, reductions can be done in the dark at n-type semiconductors, since the majority charge carrier is the electron.[26] Further, for solution redox species having $E°'$ more negative than E_{FB} of the n-type semiconductor, the redox behavior should be similar to that at metallic electrodes except for differences in the heterogeneous electron-transfer kinetics from electrode to electrode.[26] We assume that the surface chemistry of n- and p-type Si will be the same with respect to the Pt(0) interactions, which is the key reason to examine the behavior of platinized n-type Si to understand p-type Si.

n-Type Si has a flat-band potential, E_{FB}, of ~−0.3 V vs. SCE,[16] indicating that H_2 evolution should be possible in the dark at the potentials associated with $E°'(H_2O/H_2)$, since $E°'(H_2O/H_2)$ is more negative than E_{FB} for all but very acidic solutions. However, as we have previously shown, the H_2 evolution kinetics are poor.[4] Platinized n-type Si does give better current–voltage curves than the naked surface. As for Pt(0) on W, the amount of Pt(0) deposited is as close as possible to that needed to give optimum properties for platinized p-type Si. Figures 4 and 5 and Table II summarize data from several independently prepared electrodes. The current–voltage curves for H_2 evolution have been recorded as a function of pH, Figure 4, and generally reveal an onset for current close to that expected on thermodynamic grounds with current densities that exceed 1 mA/cm^2 at a potential <200 mV more negative than $E°'(H_2O/H_2)$. At the same potential for naked n-type Si the current densities for H_2 evolution is negligible.

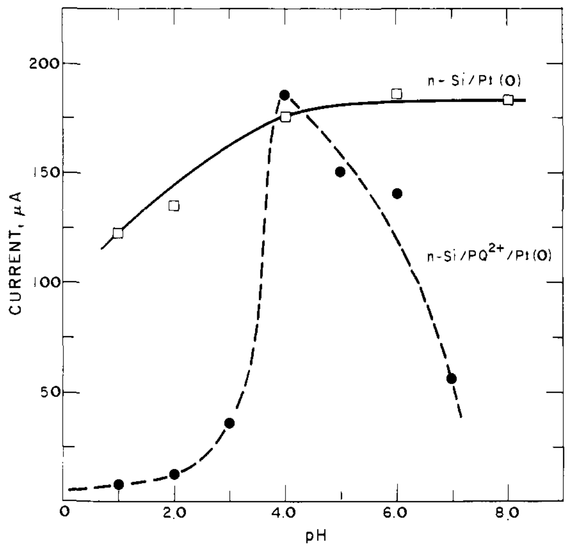

Figure 5. Steady-state current at 200 mV negative of $E°'(H_2O/H_2)$ for an n-type Si electrode directly platinized as a function of pH (□). Data are also shown for the steady-state current at 140 mV negative of $E°'(H_2O/H_2)$ for n-type Si derivatized with $[(PQ^{2+})_n{\cdot}nPt(0)]_{surf}$ (●). These data are for electrode 4 of Table II (□) and for electrode 1 of Table IV (●).

Table II. H_2 Evolution Current at 200 mV More Negative Than $E°'(H_2O/H_2)$ from Platinized n-Type Si Electrodes[a]

electrode[b]	electrolyte soln[c]	$E°'(H_2O/H_2)$, V vs. SCE	i, μA[d]
1	pH 7.0	−0.66	92
	pH 5.0	−0.54	70
	pH 3.0	−0.42	60
	pH 1.0	−0.30	50
2	pH 8.0	−0.72	270
	pH 6.0	−0.60	275
	pH 5.0	−0.54	255
	pH 4.0	−0.48	260
	pH 2.0	−0.36	200
	pH 1.0	−0.30	180
3	pH 7.0	−0.66	135
	pH 5.5	−0.57	130
	pH 4.0	−0.48	150
	pH 1.0	−0.30	100
4	pH 8.0	−0.72	180
	pH 6.0	−0.60	185
	pH 4.0	−0.48	175
	pH 2.0	−0.36	135
	pH 1.0	−0.30	122

[a] Data are taken from steady-state (10 mV/s) current-voltage curves like those shown in Figure 4. Cf. Figure 5 for a plot of i vs. pH for such electrodes. [b] Electrodes prepared from n-type Si, ~8 mm^2 exposed area. Pt(0) deposited from $PtCl_6^{2-}$ containing media; cf. Experimental Section. [c] Aqueous buffer systems are described in the Experimental Section. Solutions were stirred and Ar-purged during data collection. [d] Current for H_2 evolution measured at 200 mV more negative than $E°'(H_2O/H_2)$. The pH dependence profile is the same for other arbitrary negative potentials relative to $E°'(H_2O/H_2)$.

Though the properties of the platinized n-type Si vary from sample to sample in some respects, some generalizations can be made. First, the Pt(0) is an effective catalyst for H_2 evolution; the onset of current moves ~59 mV/pH unit as expected thermodynamically. Second, the kinetics for H_2 evolution do not appear to be as good as for platinized W or Pt. Third, there is a pH dependence on the observed current at a given potential relative to $E°'(H_2O/H_2)$, (Figure 5 and Table II). The relatively poor performance at low pH is likely due to the fact that $E°'$-

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(26) (a) Gerischer, H. In "Physical Chemistry - An Advanced Treatise", Eyring, H.; Henderson, D.; Jost, W., Eds.; Academic Press: New York, 1970; Vol. IXA, pp 467–477. (b) Frank, S. M.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 7427. (c) Kohl, P. A.; Bard, A. J. *Ibid.* **1977**, *99*, 7531. (d) Cf. also ref 17.

(H_2O/H_2) at low pH is close enough to E_{FB} that the kinetics are sluggish; apparently there is not a sufficient accumulation layer at these potentials to give good kinetics. This interpretation would be consistent with a non-uniform coating of Pt(0) where again the interface energetics are dominated by the contact of the aqueous solution with the Si/SiO_x surface and not by the contact with a uniform film of Pt(0). The relatively poor kinetics compared to platinized W are attributable to the different properties of the n-type Si and W as surfaces onto which Pt(0) is deposited. However, the kinetics for H_2 evolution at any pH studied are sufficiently good that poor kinetics for H_2 evolution at low pH cannot be the cause of lower efficiency for the platinized p-type Si at lower pH's. This conclusion is especially firm when it is considered that the difference in $E°'(H_2O/H_2)$ and E_{CB} (cf. Scheme I) can be regarded as the driving force for the reduction of H_2O by the excited electrons.[27] The $|E°'(H_2O/H_2) - E_{CB}|$ difference is analogous to the potential beyond $E°'(H_2O/H_2)$ used to attain a certain current density. The value of $|E°'(H_2O/H_2) - E_{CB}|$ is given by the difference between $E_V(\text{max})$ and E_g. Thus, at lower pH's there is more driving force for the reduction of H_2O by the excited electrons, but in no case is $|E°'(H_2O/H_2) - E_{CB}|$ less than 0.5 V, since $E_V(\text{max})$ is approximately 0.5 V and E_g is 1.1 V. At a potential of 0.5 V more negative than $E°'(H_2O/H_2)$, it is obvious that platinized n-type Si will give a very high current density for H_2 evolution.

c. Mechanism of H_2 Evolution Catalysis by Pt(0) on p-Type Si. The data for platinized n- and p-type Si lead us to conclude that at the optimum amounts of Pt(0) there is incomplete coverage of the Pt(0). We adopt the mechanism for improvement of photoelectrochemical H_2 generation to be one where the role of Pt(0) is to give an increase in the rate of the reaction of the photoexcited electrons with H_2O. In particular, the variable efficiency with pH that is due to lower E_V at lower pH reveals that there is insufficient Pt(0), or, more specifically, it is sufficiently non-uniform in coverage that the interface energetics remain dominated by the contact of the semiconductor surface with the liquid electrolyte. We hypothesize that the mechanism of the catalysis involves first photoexcitation of e^-–h^+ pairs followed by charging of small Pt(0) aggregates with the excited electrons. The charged Pt(0) aggregates equilibrate with H_2O at a sufficiently good rate, independent of pH, that this is not the limiting factor in achieving high efficiency for the photocurrent densities employed. A representation of the mechanism is shown in Scheme III.

d. Improvement of Photoelectrochemically H_2 Generation by a Redox Polymer Impregnated with Pt(0). We have recently reported preliminary results[7] showing that improvement in photogeneration of H_2 results from p-type Si first derivatized with I and then with $PtCl_6^{2-}$. We now amplify our results for this system and provide information concerning the mechanism and factors that could limit efficiency.

Catalytic photocathodes can be prepared according to the procedure represented by eq 2–4. The polymer $(PQ^{2+})_n$ is formed

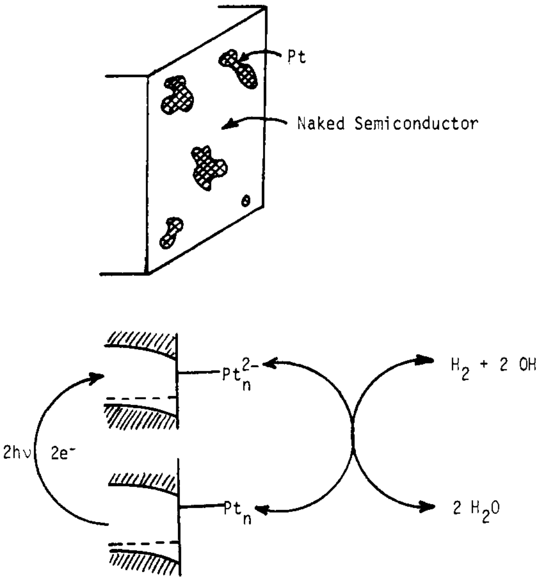
$$\text{p-Si} + n\text{I} \xrightarrow[\text{CH}_3\text{CN}]{25\ °\text{C}} \text{p-Si}/[(\text{PQ}^{2+})_n\cdot 2n\text{Br}^-]_{\text{surf.}} \quad (2)$$

$$\text{p-Si}/[(\text{PQ}^{2+})_n\cdot 2n\text{Br}^-]_{\text{surf.}} + n\text{PtCl}_6^{2-} \rightarrow \text{p-Si}/[(\text{PQ}^{2+})_n\cdot n\text{PtCl}_6^{2-}]_{\text{surf.}} + 2n\text{Br}^- \quad (3)$$

$$\text{p-Si}/[(\text{PQ}^{2+})_n\cdot n\text{PtCl}_6^{2-}]_{\text{surf.}} \xrightarrow[-0.3\text{ V vs. SCE}]{h\nu > E_g,\ 0.1\text{ M KBr}} \text{p-Si}/[(\text{PQ}^{2+})_n\cdot n\text{Pt(0)}\cdot 2n\text{Br}^-]_{\text{surf.}} + 6n\text{Cl}^- \quad (4)$$

from I via hydrolysis of the MeO–Si bonds and covalent attachment to the electrode surface is via reaction with surface-OH groups as represented in Scheme IV. Coverages of $(PQ^{2+/+\cdot})$ used in these studies are in the range 5×10^{-9} to 5×10^{-8} mol/cm^2.

Scheme III. Representation of Role of Small Amounts of Deposited Pt(0) on a p-Type Semiconductor Illuminated with $>E_g$ Light, Immersed in an Aqueous Electrolyte Solution



[a] The Pt_n particles serve to catalyze reaction of the minority carriers (e^-'s) with H_2O by becoming charged by the photoexcited electrons.

The incorporation of $PtCl_6^{2-}$ has been established by analyzing p-Si/$[(PQ^{2+})_n\cdot nPtCl_6^{2-}]_{\text{surf.}}$ surfaces using Auger spectroscopy.[7] Study[15] of the ion-exchange reaction using $IrCl_6^{2-}$ instead of $PtCl_6^{2-}$ has confirmed the essential findings with $PtCl_6^{2-}$. The $IrCl_6^{2-}$ is reversibly electroactive and persistently electrostatically bound to the $(PQ^{2+})_n$ polymer. Correlation of the electrochemical response of the bound $IrCl_6^{2-}$ and its Auger spectroscopy[15] show that our earlier assertion[7] of complete charge compensation by $PtCl_6^{2-}$ is essentially correct. We assume $IrCl_6^{2-}$ to behave like $PtCl_6^{2-}$ except that $PtCl_6^{2-}$ is much more redox labile and is easily reducible to Pt(0). Deliberate reduction of $PtCl_6^{2-}$ in the $(PQ^{2+})_n$ by illumination of the p-type Si substrate held at −0.3 V vs. SCE results in Auger-detectable Pt throughout the $(PQ^{2+})_n$ polymer using the depth-profile analysis technique. But the Pt(0) could be accumulated at the p-Si/$(PQ^{2+})_n$ interface, since merely dipping p-type Si into aqueous $PtCl_6^{2-}$ gives some improvement in H_2 evolution efficiency. Likewise, dipping W electrodes into aqueous $PtCl_6^{2-}$ yields improvement in H_2 evolution efficiency. One issue we address here, then, is the role of Pt(0) dispersed in the polymer relative to that present at the p-Si/$(PQ^{2+})_n$ interface. Some Pt(0) is expected to be at the p-Si/$(PQ^{2+})_n$ interface even on a statistical basis. The data above, section a, adequately demonstrate that Pt(0) on the p-type Si surface can improve H_2 evolution efficiency with a characteristic pH dependence.

The p-Si/$[(PQ^{2+})_n\cdot Pt(0)\cdot 2nX^-]_{\text{surf.}}$ electrodes do give a much higher efficiency for photogeneration of H_2 than does naked p-type Si. The efficiencies are generally somewhat lower than from direct platinization. Table III gives the efficiency for a number of independently prepared catalytic photocathodes as a function of pH. In every case the general effect on efficiency upon varying pH is that there is an optimum efficiency near pH 4. Efficiency is low both at high and at low pH. This result establishes that the p-Si/$[(PQ^{2+})_n\cdot nPt(0)\cdot 2nX^-]_{\text{surf.}}$ electrodes give an improvement in H_2 generation by a mechanism that differs, at least in part, from the platinized p-type Si electrodes described above. Figure 2 shows a comparison of the efficiency vs. pH profile for the two different modifications. To further contrast the two catalyst systems, the onset of photocurrent is essentially pH independent for the $[(PQ^{2+})_n\cdot nPt(0)]_{\text{surf.}}$ system, whereas the onset of photocurrent shifts with pH for the directly platinized p-type Si.

Dark behavior of n-type Si derivatized with I and then with $PtCl_6^{2-}$ and reduced to yield *n*-Si/$[(PQ^{2+})_n\cdot nPt(0)\cdot 2nX^-]_{\text{surf.}}$ confirms that there is a substantive difference compared to directly

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[27] The view that the $|E_{CB} - E°'(H_2O/H_2)|$ difference is the driving force for H_2 follows from the related hypothesis that for n-type semiconductors the $|E_{VB} - E°'(O_2/H_2O)|$ difference is the driving force from O_2 evolution: Bocarsly, A. B.; Bolts, J. M.; Cummings, P. G.; Wrighton, M. S. *Appl. Phys. Lett.* **1977**, *31*, 568.

Scheme IV. Representation of the Surface Derivatization Using Reagent I to Prepare Electrodes Bearing Polymeric Quantities of an Electroactive Reagent

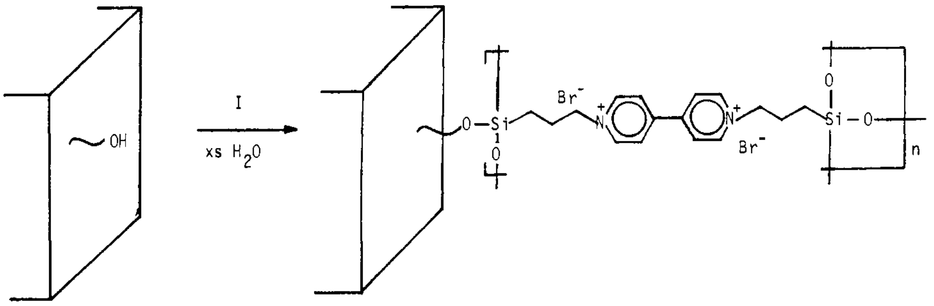


Table III. Representative Efficiencies for Conversion of 632.8-nm Light to Chemical Energy Using p-Si/[$(PQ^{2+})_n \cdot n$Pt(O)·$2nX^-$]$_{surf.}$-Based Photoelectrochemical Cells[a]

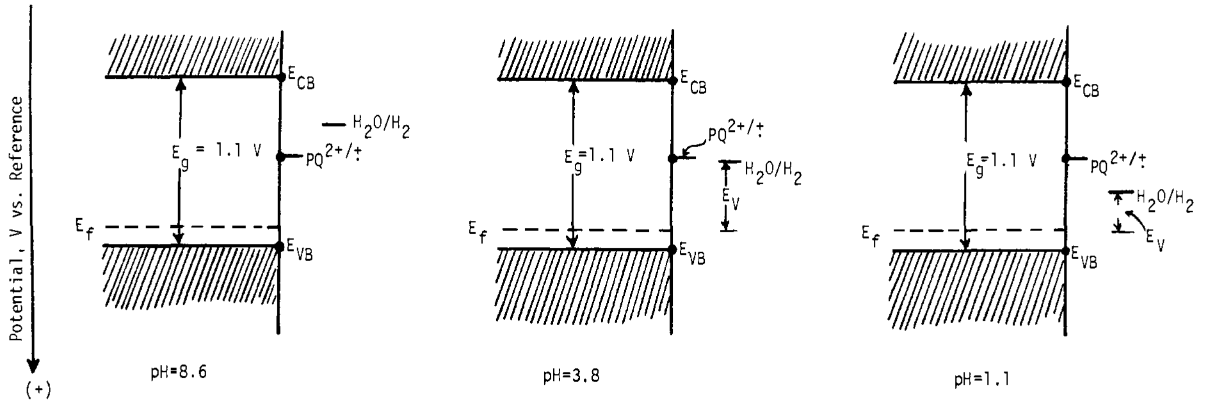
electrode[b]	electrolyte soln	$E°'(H_2O/H_2)$ V vs. SCE	input, mW/cm²	Φ_e at $E°'(H_2O/H_2)$	E_V(max), mV (E_V at η_{max}, mV)	η_{max}, %
1	H_2O, pH 5.5	−0.57	20.8	0.43	420 (160)	2.2
	pH 4.0	−0.48	20.8	0.71	400 (160)	4.1
	pH 1.0	−0.30	20.8	0.68	260 (95)	1.4
2	H_2O, pH 5.5	−0.57	11.2	0.63	360 (170)	1.8
	pH 4.0	−0.48	10.8	0.83	340 (150)	5.0
	pH 1.0	−0.30	10.9	0.53	200 (60)	0.9
3	H_2O, pH 5.5	−0.57	20.8	0.51	420 (180)	2.7
	pH 4.0	−0.48	20.8	0.81	410 (150)	3.7
	pH 1.0	−0.30	20.8	0.40	200 (75)	0.5
4	H_2O, pH 6.0	−0.60	15.1	0.19	340 (160)	1.2
	pH 5.0	−0.54	15.1	0.37	280 (120)	1.3
	pH 4.0	−0.48	15.1	0.54	280 (100)	1.6
	pH 3.0	−0.42	15.1	0.55	270 (80)	1.3
	pH 2.0	−0.36	15.1	0.64	240 (60)	0.6
	pH 1.0	−0.30	15.1	0.23	200 (40)	0.2
5	H_2O, pH 6.0	−0.60	7.1	0.19	340 (160)	1.2
	pH 5.0	−0.54	7.1	0.32	280 (120)	1.6
	pH 4.0	−0.48	7.1	0.54	280 (100)	1.8
	pH 3.0	−0.42	7.1	0.56	270 (80)	1.5
	pH 2.0	−0.36	7.1	0.62	200 (60)	0.6
	pH 1.0	−0.30	7.1	0.25	200 (40)	0.3
6	H_2O, pH 7.0	−0.66	9.4	0.09	340 (120)	0.6
	pH 5.5	−0.57	9.4	0.16	340 (140)	1.2
	pH 4.0	−0.48	9.4	0.23	340 (120)	1.4
	pH 1.0	−0.30	9.4	0.16	240 (100)	0.8
7	H_2O, pH 8.0	−0.72	6.9	0.16	460 (270)	2.3
	pH 6.0	−0.60	6.9	0.24	460 (240)	2.9
	pH 5.0	−0.54	6.9	0.36	380 (180)	2.8
	pH 4.0	−0.48	6.9	0.45	400 (170)	3.8
	pH 1.0	−0.30	6.9	0.62	260 (90)	1.8

[a] Except where noted otherwise, table headings have the same meaning as in Table I. [b] Electrodes prepared by first derivatizing with reagent I and then dispersing Pt into the $(PQ^{2+/+\cdot})_n$ polymer system by exchanging $2n$Br$^-$ with nPtCl$_6^{2-}$; see Experimental Section.

platinizing a Si surface. Data in Table IV and in Figures 4 and 5 contrast the two different H_2 evolution catalysts. The current–voltage curves for n-Si/[$(PQ^{2+})_n \cdot n$Pt(0)]$_{surf.}$ cathodes as a function of pH (Figure 4) clearly show a difference compared to platinized n-type Si. In particular, the onset of cathodic current is independent of pH for electrodes functionalized with I. The onset of current coincides with the position where $(PQ^{2+})_n$ is reduced to $(PQ^{+\cdot})_n$. Further, the H_2 evolution current at some potential arbitrarily negative of $E°'(H_2O/H_2)$ shows a pH dependence such that there is a peak in the profile at pH ~4 (Figure 5 and Table IV).

To interpret the above results regarding pH dependence we propose that the mechanism for H_2 evolution proceeds via prior reduction of $(PQ^{2+})_n$ to $(PQ^{+\cdot})_n$. Reduction of the $(PQ^{2+})_n$ to $(PQ^{+\cdot})_n$ alone is not sufficient to give improvement in H_2 photogeneration, since $(PQ^{+\cdot})_n$ does not react with H_2O despite the fact that reduction of H_2O is thermodynamically allowed for a wide range of pH's. Cyclic voltammetry for a number of reversible, metallic electrodes derivatized with I shows the $E°'(PQ^{2+/+\cdot})_n$ to be −0.55 ± 0.05 V vs. SCE independent of the substrate or pH (Table V). Thus, the reducing power of the surface $(PQ^{+\cdot})_n$ is fixed while the potential needed to evolve H_2 from H_2O moves 59 mV/pH. Importantly, we find that photoreduction of solution MV^{2+}, $E°'(MV^{2+/+\cdot}) = -0.69$ V vs. SCE, occurs with an E_V that is independent of pH in the range pH 0–7 in aqueous solution, as determined by cyclic voltammetry. That is, reduction of MV^{2+} to $MV^{+\cdot}$ at illuminated p-type Si occurs at the same potential independent of pH. For the surface $(PQ^{2+})_n$ system we also find that reduction to form $(PQ^{+\cdot})_n$ under illumination is also essentially independent of pH. The waves do sometimes vary as much as 100 mV, but generally an output voltage, E_V, in the range 300–500 mV is obtained and for a given electrode the E_V is independent of pH (within 50–100 mV) in the range pH 0–7. Whenever $E_{redox}(PQ^{2+/+\cdot})_n$ is more negative than $E_{redox}(H_2O/H_2)$ it should be possible to evolve H_2 if the rate of $(PQ^{+\cdot})_n$ reaction with H_2O can be increased. The Pt(0) incorporation procedure provides a mechanism to equilibrate $(PQ^{2+/+\cdot})_n$ with (H_2O/H_2), but only when the pH is low enough will the H_2 evolution be thermodynamically possible. Thus, the decline in efficiency at high pH's for n- and p-Si/[$(PQ^{2+})_n \cdot n$Pt(0)·$2nX^-$]$_{surf.}$ is attributable to the lack of sufficient reducing power from the $(PQ^{2+/+\cdot})_n$ system. In fact, at pH ~4, $E°'(PQ^{2+/+\cdot})_n$ is nearly the same as $E°'(H_2O/H_2)$. The low efficiency at the lower pH's is attributable to the lower E_V, since the E_V is relative to the (H_2O/H_2) couple, not relative to the $(PQ^{2+/+\cdot})_n$ couple. Scheme V gives the interface energetics as a function of pH, to illustrate

Scheme V. Representation of the Energetics of a p-Type Si Photocathode Bearing the $(PQ^{2+/+\cdot})_n$ Redox System Contacting Aqueous Electrolytes at Different pH's[a]



[a] At high pH, the formal potential of $(PQ^{2+/+\cdot})_n = -0.55$ V vs. SCE is not sufficiently negative to effect H_2 evolution efficiently. At low pH the $(PQ^{2+/+\cdot})_n$ system is sufficiently negative, but the driving force gives a low photovoltage, E_V, with respect to H_2 evolution. At the intermediate pH, the $(PQ^{2+/+\cdot})_n$ is at about the same potential as (H_2O/H_2), and H_2 evolution should proceed efficiently provided the kinetics are good for the reduction.

Table IV. H_2 Evolution Current at 140 mV More Negative Than $E°'(H_2O/H_2)$ from n-Si/$[(PQ^{2+})_n \cdot nPt(0) \cdot 2nX^-]_{surf.}$ Electrodes

electrode[a]	electrolyte soln[b]	$E°'(H_2O/H_2)$, V vs. SCE	i, μA[c]
1	pH 7.0	−0.66	55
	pH 6.0	−0.60	140
	pH 5.0	−0.54	150
	pH 4.0	−0.48	185
	pH 3.0	−0.42	35
	pH 2.0	−0.36	12
	pH 1.0	−0.30	7
2	pH 7.0	−0.66	60
	pH 6.0	−0.60	75
	pH 5.0	−0.54	180
	pH 4.0	−0.48	155
	pH 2.0	−0.36	12
	pH 1.0	−0.30	5
3	pH 8.0	−0.72	120
	pH 6.0	−0.60	190
	pH 4.0	−0.48	270
	pH 1.0	−0.30	35
4	pH 7.0	−0.66	75
	pH 5.0	−0.54	120
	pH 3.0	−0.42	70
	pH 2.0	−0.36	15
	pH 1.0	−0.30	10

[a] Electrodes were derivatized with I and then dipped into $PtCl_6^{2-}$ solution. Coverage of $(PQ^{2+})_n$ for the electrodes is in the range 5×10^{-9} to 5×10^{-8} mol/cm² and electrode areas are ~8 mm²; cf. Experimental Section. [b] Aqueous buffers prepared as described in the Experimental Section. Solutions were stirred and Ar-purged during data collection. [c] Current for H_2 evolution recorded at 140 mV more negative than $E°'(H_2O/H_2)$. Data are culled from steady-state, 10 mV/s, current-voltage curves like those shown in Figure 4. Cf. also the plot of i vs. pH in Figure 5. The current was recorded at 140 mV more negative than $E°'(H_2O/H_2)$ for convenience; i vs. pH for recording at other potentials gives the same profile as at 140 mV negative of $E°'(H_2O/H_2)$.

Table V. Electrochemical Potential of Solution and Surface-Confined *N,N'*-Dialkyl-4,4'-bipyridinium Reagents

redox system	solvent	electrode	$E°'$,[a] V vs. SCE
$(PQ^{2+/+\cdot})_{soln}$	CH_3CN	Pt, Au, n-Si	−0.45 ± 0.01
(I in soln[b])	H_2O (pH ~7)		−0.66 ± 0.01
$[(PQ^{2+/+\cdot})_n]_{surf.}$[c]	CH_3CN	Pt, Au, n-Si	−0.45 ± 0.01
(from I)	H_2O (pH 1−8.6)	Pt, Au, n-Si W, n-MoS_2	−0.55 ± 0.05
$(MV^{2+/+\cdot})_{soln}$[d]	CH_3CN	Pt, Au, n-Si	−0.45 ± 0.01
	H_2O (pH 1−7)	Hg, n-Si	−0.69 ± 0.01
	H_2O (pH 7)	Pt, Au	−0.69 ± 0.01

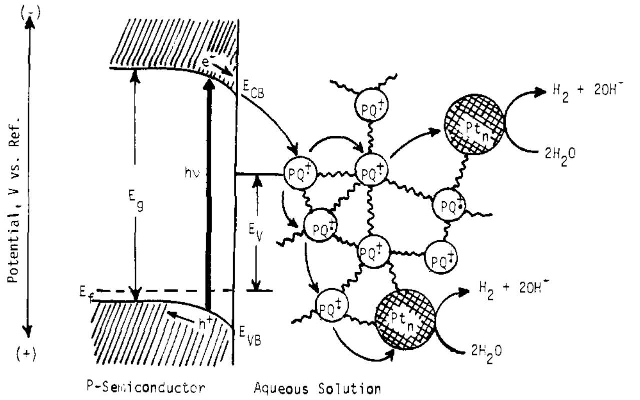
[a] $E°'$'s are taken to be the average position of the cathodic and anodic peak in a 100-mV/s cyclic voltammetry scan. In CH_3CN the supporting electrolyte is 0.1 M $[n\text{-}Bu_4N]ClO_4$ and in H_2O the electrolyte is generally 0.1−1.0 M KCl or KBr. [b] I is {*N,N'*-bis(3-(trimethoxysilyl)propyl)-4,4'-bipyridinium }dibromide; see text. Note that I hydrolyzes in H_2O solvent, but good cyclic voltammetry can be obtained for fresh solutions. [c] Surface-confined material from derivatization of electrode surfaces with I. The data given are representative. The $E°'$ is constant, ±0.05 V, over the pH range indicated and for a wide range of electrolyte (KCl or KBr) concentrations. [d] *N,N'*-Dimethyl-4,4'-bipyridinium.

the situation; $E_{redox}(PQ^{2+/+\cdot})_n$ must be more negative than $E_{redox}(H_2O/H_2)$ but not so negative that E_V for H_2 evolution is low. As we find experimentally, the optimum pH would be expected to be near where $E°'(PQ^{2+/+\cdot})_n$ equals $E°'(H_2O/H_2)$.

A value of E_V that is independent of pH for a p-Si/SiO_x surface is perhaps surprising in view of the general finding that there is a 59 mV/pH shift in the value of E_{FB}. However, as previously reported[6] for p-InP where a shift in E_{FB} with pH might be expected to give variations in E_V for the $MV^{2+/+\cdot}$ couple, the E_V measured is relative to the redox couple $(PQ^{2+/+\cdot})_n$ or $MV^{2+/+\cdot}$ whose $E°'$ is such that Fermi level pinning applies. In the absence of a redox couple with which the semiconductor equilibrates, the usual effects of pH on E_{FB} might be expected, but here we employ a fast redox couple that does equilibrate with the semiconductor.

A complication with the $[(PQ^{2+})_n \cdot nPt(0)]_{surf.}$ system on p-type Si compared to $(PQ^{2+})_n$ without the Pt(0) is that the clean, fast redox chemistry of $(PQ^{2+/+\cdot})_n$ is significantly altered by the presence of the Pt(0), especially after running steady-state current−voltage curves. The observation is that the wave for the photoreduction $(PQ^{2+})_n \rightarrow (PQ^{+\cdot})_n$ is typically shifted more negative by at least 100 mV and the return wave $(PQ^{+\cdot})_n \rightarrow (PQ^{2+})_n$ is significantly broadened and shifted more positive after incorporation of Pt(0). In the extreme, cyclic voltammetry waves essentially disappear though the polymer remains attached to the surface. These observations suggest that the oxide layer, SiO_x, between the bulk Si and the polymer overlayer[7] grows during use. This can contribute to loss in efficiency with prolonged use. Experiments with electrodes such as Pt, Au, MoS_2, and W coated with $[(PQ^{2+})_n \cdot nPt(0)]_{surf.}$ do not exhibit adverse effects from incorporation of the Pt(0) into the $(PQ^{2+})_n$ system (vide infra), supporting the conclusion that it is the SiO_x layer that is changing with use of p-type Si. This point will be elaborated in future experimentation. The important point is that the incorporation of Pt(0) does not appear to alter the $E°'$ for $(PQ^{2+/+\cdot})_n$. The pH dependence for H_2 evolution on both n- and p-type Si accords well with an $E°'$ for the $(PQ^{2+/+\cdot})_n$ of −0.55 V vs. SCE.

Considering that $E°'$ for I dissolved in H_2O is −0.66 V vs. SCE and the related $MV^{2+/+\cdot}$ system is at −0.69 V vs. SCE (Table V), Scheme VI. Representation of the Mechanism of Catalyzed H_2 Evolution from an Illuminated p-Type Semiconductor Modified with $[(PQ^{2+})_n{\cdot}nPt(0)]_{surf.}$ Contacting an Aqueous Electrolyte Solution[a]



[a] The photovoltage, E_V, is the difference in E_f and $E^{\circ\prime}(H_2O/H_2)$. The arrows show the flow of electrons indicating that the Pt_n particles come into equilibrium with the reduced PQ^{2+}.

it is noteworthy that the surface-confined material from I has an $E^{\circ\prime}$ that is only −0.55 V vs. SCE. Generally, the $E^{\circ\prime}$ for a surface-attached species is close to its solution analogue.[28] In this case the relatively large discrepancy may be due to the fact that the surface *N,N'*-dialkyl-4,4'-bipyridinium species may interact in the reduced form, since reversible dimerization is known to occur for high concentrations of such reagents in solution.[29a] With respect to the H_2 evolution, the less negative $E^{\circ\prime}$ on the surface means that the optimum pH is lower than would be predicted based on the $E^{\circ\prime}$'s for the solution species.

Our proposed mechanism for H_2 evolution from illuminated p-Si/$[(PQ^{2+})_n{\cdot}nPt(0){\cdot}2nX^-]_{surf.}$ is represented by eq 5 and 6 and

$$\text{p-Si}/[(PQ^{2+})_n{\cdot}nPt(0)]_{surf.} \xrightarrow{h\nu > E_g} \text{p-Si}/[(PQ^{+\cdot})_n{\cdot}nPt(0)]_{surf.} \tag{5}$$

$$\text{p-Si}/[(PQ^{+\cdot})_n{\cdot}nPt(0)]_{surf.} + nH_2O \rightarrow 1/2nH_2 + nOH^- + \text{p-Si}/[(PQ^{2+})_n{\cdot}nPt(0)]_{surf.} \tag{6}$$

by Scheme VI. There is undoubtedly some component of the photocurrent that is a consequence of the Pt(0) contacting the semiconductor surface, but the pH dependence seems to rule out a dominant role for the Pt(0) at the interface. However, the decline in efficiency at the higher pH's is less pronounced at low light intensities where low current densities result. Apparently, the small amount of Pt(0) at the interface can support a low current density with a pH profile like that for surfaces that are directly platinized. At higher light intensities the contribution to the photocurrent by the small amount of Pt(0) at the interface is relatively small, analogous to suboptimum amounts of Pt(0) directly deposited onto p-type Si (vide supra).

Statistically it is, of course, likely that some Pt(0) will contact the Si/SiO_x layer when Pt(0) is dispersed into the $(PQ^{2+})_n$. However, this is not the only source of a significant efficiency for H_2 evolution at high pH's. One possibility is that there is mediation of H_2O reduction via the formation of $(PQ^0)_n$ formed by further reduction of $(PQ^{+\cdot})_n$. The $E^{\circ\prime}(PQ^{+\cdot/0})_n$ is ~0.4 V more negative[14] than $E^{\circ\prime}(PQ^{2+/+\cdot})_n$, and $(PQ^0)_n$ would therefore be capable of reducing H_2O to H_2 at significantly higher pH's than would $(PQ^{+\cdot})_n$. The $(PQ^0)_n$ is accessible since the p-Si is Fermi level pinned in this potential regime.[11] Unfortunately, studies at high pH's are precluded by the decomposition of the $(PQ^{2+})_n$ system. The decomposition is likely base-induced hydrolysis of the –Si–O–Si– linkages of the polymer as well as nucleophilic attack by OH^- as is found for MV^{2+}.[29b] Another conceivable complication is that the $(PQ^{+\cdot})_n \rightleftarrows (PQ^0)_n$ system is not reversible, since $(PQ^0)_n$ may suffer irreversible reactions as does the MV^0 system in aqueous solution. However, we do find some electrodes that do exhibit reversible and persistent $(PQ^{+\cdot})_n \rightleftarrows (PQ^0)_n$ cyclic voltammetry waves in H_2O/electrolyte solution. The wave position on a reversible electrode material is at ~−0.9 V vs. SCE, consistent with expectation. This would suggest another peak in the efficiency vs. pH profile to occur in the pH ~10 range, if the surfaces were durable. In any event, the separation of ~400 mV for the $E^{\circ\prime}$'s for $(PQ^{2+/+\cdot})_n$ and $(PQ^{+\cdot/0})_n$ could allow for a nonzero H_2 evolution efficiency at the pH's where the rate from $(PQ^{+\cdot})_n$ would be expected to be very low. If the $(PQ^0)_n$ equilibrates rapidly with H_2O via the dispersed Pt(0), it is possible that the durability of $(PQ^0)_n$ would be quite good. The rate of catalyzed oxidation of $(PQ^0)_n$ by H_2O must dominate the rate of irreversible reaction of $(PQ^0)_n$ that leads to its consumption. Whatever the role for $(PQ^0)_n$, the pH profile for efficiency from the $[(PQ^{2+})_n{\cdot}nPt(0)]_{surf.}$ system shows that the mechanism is not dominated by Pt(0) directly at the Si/SiO_x interface as for the electrodes that are directly platinized.

Another issue that should be mentioned here is that the potential of the surface $(PQ^{2+/+\cdot})_n$ system on photocathodes will be a function of light intensity and E_f. In the dark, for example, it is not possible to reduce $(PQ^{2+})_n$ to $(PQ^{+\cdot})_n$ because the p-type semiconductor is blocking in the dark to reductions. At very low light intensities the surface polymer may behave as if there is an infinite reservoir of reducible material and the $(PQ^{2+})_n$ may not be converted significantly to $(PQ^{+\cdot})_n$. In any event, the peak in the $(PQ^{2+})_n \rightarrow (PQ^{+\cdot})_n$ photocurrent–voltage curve may be much more negative than at high light intensity. Thus, the reducing power of $(PQ^{2+/+\cdot})_n$ available at a given electrode potential, E_f, will depend on light intensity. But at a given light intensity the pH vs. efficiency profile should still be controlled by the fact that $E^{\circ\prime}(PQ^{2+/+\cdot})_n$ is pH independent and fixed to −0.55 V vs. SCE. Whether the actual $E_{redox}(PQ^{2+/+\cdot})_n$ will be at this value depends on light intensity and E_f. Likewise, whether there is any significant amount of $(PQ^0)_n$ present depends on light intensity and E_f. Similar arguments concerning the E_{redox} of surface reagents have been made for ferrocene-based materials on the surface of photoanodes.[30]

Another vein of experimentation that supports our mechanistic proposal concerns the study of $Ru(NH_3)_6^{3+}$ reduction at illuminated p-Si/$[(PQ^{2+})_n]_{surf.}$ electrodes with and without Pt(0) present. The reduction of $Ru(NH_3)_6^{3+}$ is pH independent; $E^{\circ\prime}(Ru(NH_3)_6^{3+/2+})$ = −0.2 V vs. SCE.[30] Thus, the photogenerated $(PQ^{+\cdot})_n$ should be capable of reducing $Ru(NH_3)_6^{3+}$. Establishing that the modified photocathode will reduce $Ru(NH_3)_6^{3+}$ at high pH's, where H_2 evolution is inefficient, shows that the pH dependence on H_2 evolution is not due to pH effects on the redox properties (energetics, kinetics) of the $[(PQ^{2+})_n{\cdot}nPt(0)]_{surf.}$ system. Figure 6 illustrates representative photocurrent–voltage curves vs. pH. With respect to $Ru(NH_3)_6^{3+}$ reduction, the key finding is that reduction current grows at pH 6.5 when 0.1 M $Ru(NH_3)_6^{3+}$ is added to the solution. Thus, when the $(PQ^{+\cdot})_n$ system is observed to only inefficiently produce H_2 because of thermodynamic factors, the $Ru(NH_3)_6^{3+}$ is reducible. Data below establish that the rate constant for the reaction represented by eq 7 is large enough that

$$(PQ^{+\cdot})_n + nRu(NH_3)_6^{3+} \xrightarrow{k_{et}} (PQ^{2+})_n + nRu(NH_3)_6^{2+} \tag{7}$$

the 0.1 M $Ru(NH_3)_6^{3+}$ should, in fact, give a current as great as at pH 2 where H_2 is being evolved. In some cases, the current for $Ru(NH_3)_6^{3+}$ reduction at high pH more nearly approximates the photocurrent for H_2 evolution at low pH.

Variation in behavior from electrode to electrode likely reflects changes in the absolute coverage, the uniformity of coverage in the $(PQ^{2+})_n$ system, the nature and thickness of the SiO_x layer, and how much Pt(0) is actually at the interface. A number of

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[28] (a) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135. (b) Lenhard, J. R.; Murray, R. W. *J. Electroanal. Chem.* **1978**, *100*, 5213.

[29] (a) Kosower, E. M.; Cotter, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5524. (b) Farrington, J. A.; Ledwith, A.; Stam, M. F. *Chem. Commun.* **1969**, 259; Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.

[30] Bocarsly, A. B.; Walton, E. G.; Bradley, M. G.; Wrighton, M. S. *J. Electroanal. Chem.* **1979**, *100*, 283.

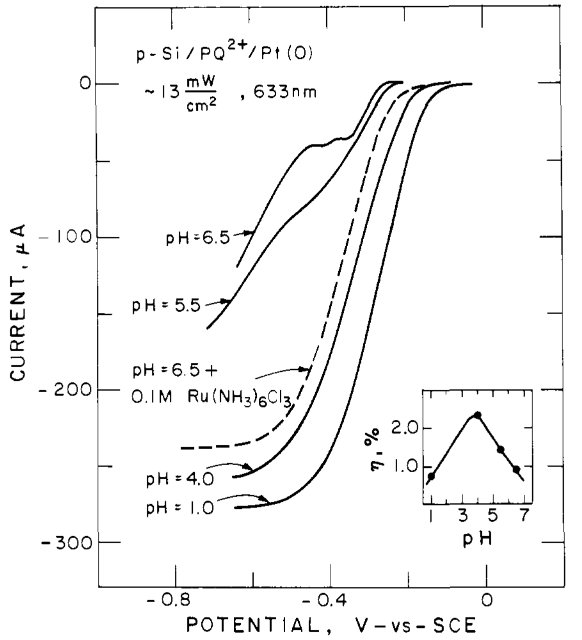

Figure 6. Steady-state (10 mV/s) photocurrent–voltage curves for a ~0.1 cm^2 p-type Si electrode bearing $[(PQ^{2+})_n \cdot nPt(0)]_{surf.}$ as a function of pH. The dashed curve is the photocurrent–voltage curve for mediated $Ru(NH_3)_6{}^{3+}$ reduction, eq 7 of text, at pH 6.5. The inset at the lower right shows the efficiency for H_2 generation (eq 1), culled from the photocurrent–voltage curves.

experiments on independently prepared electrodes support the general conclusion that the photocurrent for $Ru(NH_3)_6{}^{3+}$ reduction increases well beyond that for H_2O reduction at the higher pH's. These experiments tend to rule out artificial sources of inefficiency for the H_2O reduction at high pH.

Study of the mediated reduction of $Ru(NH_3)_6{}^{3+}$ (in the dark) by the $[(PQ^{2+/+\cdot})_n \cdot nPt(0)]_{surf.}$ catalyst on n-type Si confirms the conclusions for p-type Si. We find that at high pH, where $(PQ^{+\cdot})_n$ is not a sufficiently powerful reductant to reduce H_2O, the reduction current for the $Ru(NH_3)_6{}^{3+}$ is as good as at low pH for an n-type Si electrode bearing $(PQ^{2+/+\cdot})_n$ but no Pt(0). Further, where the $[(PQ^{2+/+\cdot})_n \cdot nPt(O)]_{surf.}$ catalyst is working only inefficiently for H_2O reduction (high pH), the $Ru(NH_3)_6{}^{3+}$ reduction current is just as high as at low pH for the situation where only $(PQ^{2+/+\cdot})_n$ is present. Again, these results show that the diminution in H_2 evolution efficiently as pH is increased is not due to artifacts. Rather, the data for mediated reduction of $Ru(NH_3)_6{}^{3+}$ show the $[(PQ^{2+/+\cdot})_n \cdot Pt(0)]_{surf.}$ to remain an effective mediator system for reductions where the energetics and kinetics are favorable.

e. Durability and Reproducibility of the $[(PQ^{2+})_n \cdot nPt(0)]_{surf.}$ Catalyst on Si Electrodes. As in direct platinization, the $[(Pt^{2+})_n \cdot nPt(0)]_{surf.}$ catalyst system does not lead to indefinitely stable output parameters. Generally, deleterious changes in photoelectrochemical output do occur. For the various measurements given in Table III the electrodes are certainly durable on the time scale required to obtain the steady-state (10 mV/s) photocurrent–voltage curves from which the data are culled. It is possible to scan a number of such curves from 0.0 V vs. SCE to -0.7 V vs. SCE (cf. Figure 6), for example, without change in parameters after an initial "break in" of the photoelectrode. Assuming that the only mechanism for H_2 evolution is according to (5) and (6), we can easily demonstrate tens of thousands of molecules of H_2 generated per PQ^{2+} unit or Pt(0) atom on the surface. When the photoelectrode is held at a fixed potential, say -0.3 V vs. SCE at pH 4, the photocurrent for H_2 evolution at a ~15 mW/cm^2 632.8-nm input generally declines, rapidly at first, say to ~75% of the original value within 30 min, and then more slowly. After such an experiment the steady-state photocurrent–voltage curves reflect deterioration of output, but performance remains above that for the naked p-type Si. Turnover numbers for the $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$ have been demonstrated to be $>10^5$. Possible mechanisms for deterioration include aggregation of the dispersed Pt(0) and changes in the SiO_x layer between the bulk Si and the surface polymer. Significant improvement in H_2 evolution can be sustained for long periods, but constant efficiency is not yet attainable.

One set of experiments with $n\text{-}Si/[(PQ^{2+})_n \cdot nPt(0)]_{surf.}$ establishes the failure mechanism to not involve loss of the $(PQ^{2+/+\cdot})_n$. The first experiment is to examine the cyclic voltammetry at pH 8.0 before and after evolving H_2 for a period of time long enough to observe a decline in current. The electrodes used were first established to have a H_2 current/pH profile like those in Table IV and Figure 5 to ensure that the mechanism for H_2 generation involves prior reduction of $(PQ^{2+})_n$ and is not dominated by Pt(0) at the interface. The cyclic voltammetry at pH 8.0 reveals the electrochemical response of the $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$ to be unaffected by evolving H_2 at pH 4.0 at -0.6 V vs. SCE. However, during the period when H_2 was evolved the current dropped by ~50% after passing ~10^3 electrons per (PQ^{2+}) center, and the pH profile after the current–time experiment showed less of a peak at pH ~4 compared to the fresh electrode. These results suggest that the Pt(0) dispersed in the polymer is deactivated, perhaps by aggregation. This is confirmed by the ability to rejuvenate the initial properties by reincorporation of Pt(0) by a single exchange with $PtCl_6{}^{2-}$ followed by reduction to yield Pt(0).

Reproducibility of the photosensitive p-type Si interfaces is generally quite good at the stage where $(PQ^{2+})_n$ is bound to the surface. The peak of the photoreduction wave of the 5×10^{-9} to 5×10^{-8} mol/cm^2 of (PQ^{2+}) occurs at 0.0 to ~-0.2 V vs. SCE at 632.8 nm illumination intensities of ~50 mW/cm^2. Such electrodes are very durable provided that O_2 is not allowed to react with the $(PQ^{+\cdot})_n$. The largest uncontrollable factor in preparing reproducible Pt(0)-containing polymers seems to be associated with the SiO_x layer and its possible growth and reaction with the Pt(0). This issue requires further work and will be the object of continuing studies.

f. Direct Observation of Equilibration of $(PQ^{2+/+\cdot})_n$ with H_2O/H_2 via Dispersed Pt(0). Two important qualitative experiments provide direct evidence for the role of Pt(0) represented by the mechanism sketched in Scheme VI. The first concerns the p-type Si functionalized with I and I + Pt(0), and the second concerns the use of glass, as a representative insulator, functionalized with I and I + Pt(0).

The experiment with p-type Si that is crucial is to examine the cyclic voltammetry associated with the dark oxidation of the photogenerated $(PQ^{+\cdot})_n$. The $(PQ^{2+})_n$ can be reduced to $(PQ^{+\cdot})_n$ only under conditions where the minority carrier (e^-'s) are excited to the conduction band of Si by $\geq E_g$ light and the electrode potential E_f is more negative than ~0.0 V vs. SCE, eq 5. Thus, producing $(PQ^{+\cdot})_n$ requires two stimuli, light and potential. The oxidation of $(PQ^{+\cdot})_n$, though, can be effected in the dark at sufficiently positive potentials, since the process requires a majority carrier (h^+) from the p-Si, eq 8. However, the $(PQ^{+\cdot})_n$ can be oxidized by solution oxidants as was previously shown for oxidants such as ferricenium[14] and horseheart ferricytochrome *c*.[31] In the present case, we are concerned with whether H_2O can be reduced according to eq 6. Whether the process of oxidation of $(PQ^{+\cdot})_n$ by H_2O occurs can be determined by measuring the amount of charge passed corresponding to dark oxidation of $(PQ^{+\cdot})_n$, according to eq 8, as a function of reaction time.[14,31] Thus, by linear sweep voltammetry we can determine whether $(PQ^{+\cdot})_n$ is oxidized by H_2O in the dark. In the pH range 1.1–5.5 we find no dark oxidation of $(PQ^{+\cdot})_n$ on p-Si by H_2O in the absence of Pt(0). No reaction with H_2O occurs, despite the fact that the reaction is downhill, owing to slow kinetics. However, for electrode surfaces into which Pt(0) has been dispersed in the $(PQ^{2+/+\cdot})_n$ polymer, we do find that the photogenerated $(PQ^{+\cdot})_n$ does react in the pH

$$p\text{-}Si/[(PQ^{+\cdot})_n]_{surf.} \xrightarrow[E_f \text{ sufficiently positive}]{\text{dark or light}} p\text{-}Si/[(PQ^{2+})_n]_{surf.} \qquad (8)$$

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(31) Lewis, N. S.; Wrighton, M. S. *Science* **1981**, *211*, 944.

range 1.1–5.5. The result is qualitative, but compelling, support for a role for Pt(0) in equilibrating $(PQ^{+\cdot})_n$ with H_2O. At pH ~5.5 the rate of $(PQ^{+\cdot})_n$ consumption via equilibration with H_2O is slow enough to be studied with cyclic voltammetry, since the driving force is low. The rate of oxidation of $(PQ^{+\cdot})_n$ by H_2O (pH $\leq$4.5) when catalyzed by the Pt(0) is sufficiently fast that a current for H_2 generation of >10 mA/cm^2 can be accommodated by this mechanism. This limit is established by determining the rate of consumption of $(PQ^{+\cdot})_n$ due to oxidation by H_2O; cf. ref 33c for similar treatment. At lower pH's the rate is so fast that cyclic voltammetry is not useful and some other technique must be used to monitor the time dependence of $(PQ^{+\cdot})_n$ in the dark. We are now carrying out experiments using optical detection that may allow measurement of the rate of equilibration of $(PQ^{+\cdot})_n$ at pH's where we observe optimum conversion efficiency.

The experiments described above are equivocal in at least one respect. We cannot be certain that it is the Pt(0) randomly dispersed in the polymer that is the effective catalyst. It may well be that Pt(0) at the interface between the electronic conductor (Si/SiO_x) and the polymer is responsible for reaction; that is, the $(PQ^{+\cdot})_n$ may equilibrate with the Pt(0) via equilibration with the electronic conductor (SiO_x) that is in contact with the Pt(0). The second qualitative experiment that shows a role for the dispersed Pt(0) is compelling. Pyrex glass treated with I results in the attachment of $(PQ^{2+})_n$ in significant quantities. This is easily established by functionalizing the inside of a test tube by reaction of ~1 mM I in CH_3CN at 25 °C for several hours, washing with generous amounts of CH_3CN and then with H_2O, and then adding a H_2O solution of $S_2O_4^{2-}$ to the test tube. The $S_2O_4^{2-}$ reduces the $(PQ^{2+})_n$ to $(PQ^{+\cdot})_n$ as detected by the change from a colorless to purple interior surface of the test tube. The reaction is reversed upon exposure to oxidants in solution such as O_2 from air. Addition of an aqueous solution of ~1 mM K_2PtCl_6 to the test tube functionalized with I followed by washing with copious amounts of H_2O presumably results in a surface bearing $[(PQ^{2+})_n \cdot nPtCl_6^{2-}]_{surf.}$ by analogy to results described above. Treatment of this surface with aqueous H_2 yields reduction to $[(PQ^{+\cdot})_n \cdot nPt(0)]$ as evidenced by the purple coloration. Rinsing with KCl and exposure to air yields $[(PQ^{2+})_n \cdot nPt(0) \cdot 2nCl^-]_{surf.}$. The interesting experimental finding with this surface is that filling the test tube with pH 8.9 aqueous solution followed by exposure to 1 atm H_2 results in immediate purple coloration of the surface. A similar experiment for a test tube bearing $(PQ^{2+})_n$, but no Pt(0), results in no purple coloration. Further, no purple coloration develops for an aqueous solution at pH 1.1 even with Pt(0) present. The purple coloration at pH 8.9 disappears upon removal of the H_2 pressure and addition of deoxygenated acid or upon exposure to O_2. The conclusion is that the dispersed Pt(0) allows equilibration with the H_2O/H_2 couple. At pH 8.9 the H_2 is a sufficiently powerful reductant that $(PQ^{2+})_n$ can be reduced to the purple $(PQ^{+\cdot})_n$ whereas at pH 1.1 H_2 is not sufficient to reduce $(PQ^{2+})_n$. Furthermore, at pH 8.9 it is noteworthy that the $(PQ^{2+}/^{+})_n$ system is durable under H_2 and is not, apparently, irreversibly reduced to a 4,4′-bipiperidinium polymer.[32] It is, of course, possible that the PQ^{2+} in the immediate vicinity of Pt is hydrogenated; this may be a contributor to declining efficiencies in extended runs with the $p\text{-}Si/[(PQ^{2+})_n \cdot nPt(0)]_{surf.}$ electrodes. But gross hydrogenation is inconsistent with the electrochemical experiments detailed above.

g. Behavior of Tungsten, Platinum, Gold, and n-Type MoS_2 Electrodes Modified with the $[(PQ^{2+})_n \cdot nPt(0)]_{surf.}$ System. In order to gain more information concerning the properties of the $[(PQ^{2+})_n \cdot nPt(0)]_{surf.}$ catalyst, surfaces of W, Pt, Au, and n-type MoS_2 electrodes have been functionalized with reagent I according to the procedure given in the Experimental Section. Cyclic voltammograms of a functionalized W electrode in aqueous solution at several pH's are shown in Figure 7. Independent of pH, the $(PQ^{2+/+\cdot})_n$ system exhibits persistent cyclic voltammograms at a potential consistent with the reversible $(PQ^{2+})_n \rightleftarrows (PO^{+\cdot})_n$ redox system (Table V). Even at fairly low pH the reduction of the $(PQ^{2+})_n$ system is observable. The naked W has sufficiently high overvoltage for H_2 evolution (see Figure 3) that little background current for H_2 evolution is expected, and the additional surface functionalization by reagent I likely worsens the properties for H_2 evolution. Derivatization of Pt or Au with reagent I definitely does increase the overvoltage for H_2 evolution. This is especially obvious for Pt where it is possible to observe cyclic voltammetry waves for the $(PQ^{2+/+\cdot})_n$ system at low pH. At such low pH's the current density for H_2 evolution at naked Pt is far too great to be able to observe the wave for $(PQ^{2+/+\cdot})_n$.

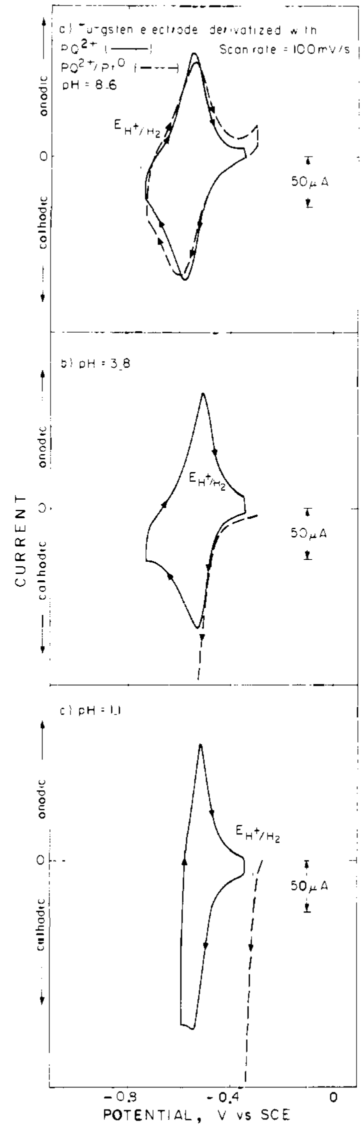

Figure 7. Cyclic voltammetry of W electrodes derivatized with $(PQ^{2+})_n$ (—) (~5.4 × 10^{-9} mol/cm^2), and $[(PQ^{2+})_n \cdot nPt(0)]$ (- - -) in (a) pH 8.6, (b) pH 3.8, and (c) pH 1.1 electrolyte. The scan rate used is 100 mV/s.

As discussed above, the formal potential of the $(PQ^{2+/+\cdot})_n$ is such that only for pH <5 should the $(PQ^{+\cdot})_n$ be a strong enough reductant to reduce H_2O to H_2 at standard conditions. Even for pH <5, however, H_2 evolution does not follow formation of $(PQ^{+\cdot})_n$, since the rate for the reduction of H_2O by $(PQ^{+\cdot})_n$ is too slow. However, as for p-type Si functionalized with the $(PQ^{2+/+\cdot})_{surf.}$ system, it is possible to replace the halide counterions by $PtCl_6^{2-}$ and to subsequently reduce the $PtCl_6^{2-}$ to Pt(0) to give a highly dispersed Pt(0) species, apparently capable of catalyzing the reaction of $(PQ^{+\cdot})_n$ with H_2O. Figure 7 includes data for the W electrode after treatment to include the Pt(0). At pH 8.6 the reduced $(PQ^{+\cdot})_n$ is incapable of reducing H_2O on thermodynamic grounds and the reversible $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$ system is detectable by cyclic voltammetry. However, for pH <5 additional current is detectable at the potential where the $(PQ^{2+})_n$ is reduced. The Pt(0) is apparently effectively incorporated and catalyzes the

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(32) Keller, P.; Moradpour, J. *J. Am. Chem. Soc.* **1980**, *102*, 7193.

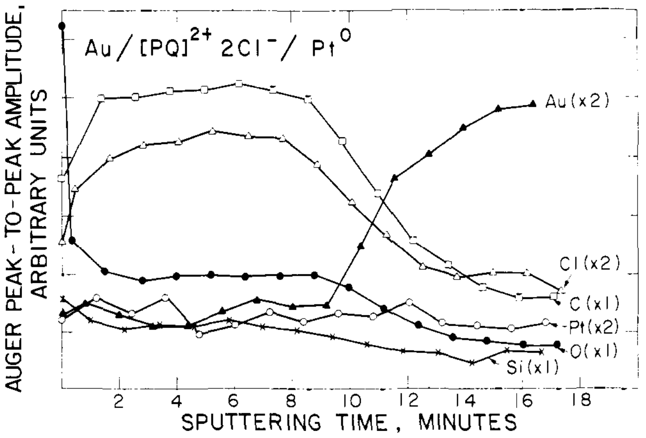


Figure 8. Auger/depth profile analysis of Au functionalized with $[(PQ^{2+})_n\cdot 2nBr^-]_{surf.}$ ($\sim 6.5 \times 10^{-8}$ mol/cm^2), anion exchanged to replace $2nBr^-$ by $nPtCl_6^{2-}$, and then treated to electrochemically reduce $PtCl_6^{2-}$.

reaction between $(PQ^{+\cdot})_n$ and H_2O to generate H_2. After running several steady-state current–voltage curves at pH 1.1 and 3.8 where H_2 evolution is observed, the cyclic voltammetry characteristic of the $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$ system is still observable and unchanged at pH 8.6.

The treatment to include Pt(0) in the $(PQ^{2+})_n$ polymer obviously leads to a significant improvement in the H_2 evolution kinetics for the W electrode. Similar improvement also results for Pt and Au electrodes derivatized with I and then treated to include Pt(0). However, as for p-type Si above, we find that merely dipping the naked (nonderivatized) W electrodes into a solution containing $PtCl_6^{2-}$ results in significant (albeit sometimes short-lived) improvement in H_2 evolution kinetics. Accordingly, as for p-type $Si/[(PQ^{2+})_n\cdot nPt(0)]_{surf.}$,[7] we have monitored the Auger spectrum of $M/[(PQ^{2+})_n\cdot nPt(0)]_{surf.}$ (M = Au, Pt, W) while sputtering the surface with reactive Ar ions (Figure 8). The depth profile analysis shows a relatively constant composition of the surface polymer as a function of depth until the polymer is completely sputtered away to reveal only bulk M. The Pt signal is weak, but observable, at about constant intensity until the polymer has been completely sputtered away. Importantly, these data show that Pt is dispersed throughout the polymer overlayer and is not only accumulated at the M/polymer interface.

However, from Figure 7 it is apparent that Pt(0) at the W/polymer or Au/polymer interface must play a more important role than at the Si/polymer interface. This conclusion is based on the observation that the onset of cathodic current for H_2 evolution depends on pH whereas on $n\text{-}Si/[(PQ^{2+})_n\cdot nPt(0)]_{surf.}$ the cathodic current onsets at the potential where $(PQ^{2+})_n$ is reduced, independent of pH. This does not mean that the Pt(0) dispersed in the polymer on Au or W is inactive. Rather, the interface Pt(0) has relatively greater importance. When H_2 is being evolved from electrodes bearing $[(PQ^{2+})_n\cdot nPt(0)]_{surf.}$, the $(PQ^{2+})_n$ is observed to be reduced to $(PQ^{+\cdot})_n$ at the usual potential. The reduction is observable to the naked eye, since the $(PQ^{2+})_n$ is colorless while the $(PQ^{+\cdot})_n$ is purple. This experiment shows that the $(PQ^{2+})_n$ remains electroactive when H_2 is being generated. For acid solution where $(PQ^{+\cdot})_n$ is a sufficiently powerful reductant to reduce H_2O, the removal of the electrode from potentiostatic control leads to the rapid disappearance of the $(PQ^{+\cdot})_n$ presumably because of the equilibration of $(PQ^{+\cdot})_n$ with H_2O via the dispersed Pt(0). At pH's where $(PQ^{+\cdot})_n$ is not capable of reducing H_2O the purple coloration of $(PQ^{+\cdot})_n$ persists indefinitely for electrodes removed from potentiostatic control in the absence of O_2 or other impurity oxidants. These experiments establish a role for the $[(PQ^{2+/+\cdot})_n\cdot Pt(0)]_{surf.}$ catalyst system, but its relative importance vs. the interface Pt(0) is less on Pt, Au, and W than for Si electrodes.

Additional confirmation of an important role for polymer bound Pt(0) comes from a set of experiments with n-type MoS_2. Dipping naked n-type MoS_2 electrodes into a typical $PtCl_6^{2-}$ solution used for the ion-exchange reaction yields an electrode having only very small current densities for H_2 evolution at pH 1.0 or 4.0; that is, unlike the other surfaces, the electrodeless plating from $PtCl_6^{2-}$ alone does not yield enough Pt(0) to effectively catalyze H_2 evolution. However, functionalization of n-type MoS_2 with I following by dipping into the $PtCl_6^{2-}$ solution yields an electrode surface from which H_2 evolution is quite good (>15 mA/cm^2 at $\sim$100 mV more negative then $E^{\circ\prime}(H_2O/H_2)$) at pH 1.0 or 4.0. The $(PQ^{2+/+\cdot})_n$ system on n-type MoS_2 exhibits essentially reversible electrochemistry in the dark since the flat band potential for n-type MoS_2 is $\sim$+0.3 V vs. SCE, placing the $E^{\circ\prime}(PQ^{2+/+\cdot})_n$ well in the conduction band.[17] The poor kinetics for H_2 evolution from naked n-type MoS_2 is a result consistent with findings for the related material p-type WSe_2 that was found to have poor H_2 evolution kinetics under illumination.[3]

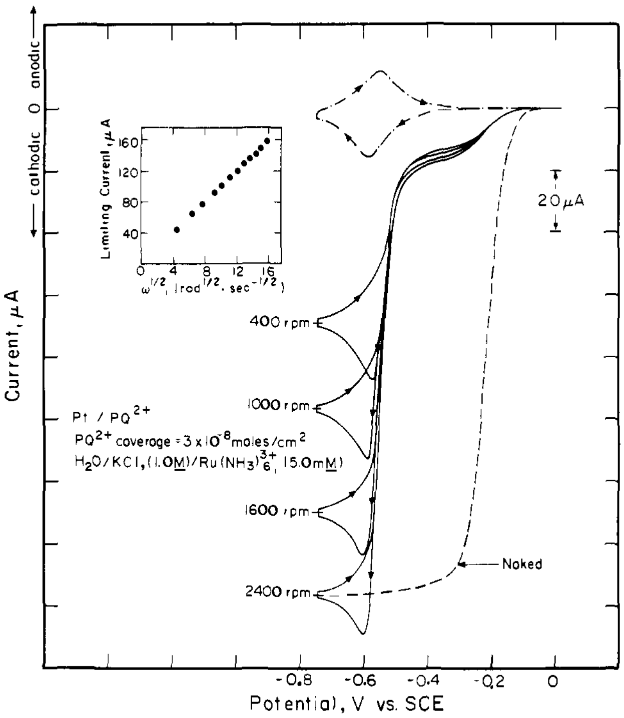
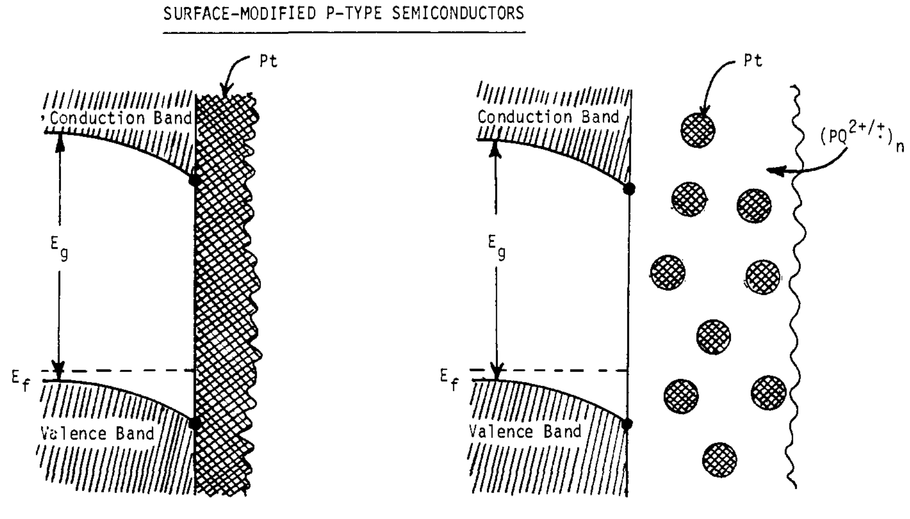


Figure 9. Steady-state current–voltage curves (at 10 mV/s) for a rotated Pt disk electrode (diameter 3 mm), naked (---), and derivatized (—) with $(PQ^{2+})_n$ in aqueous 1.0 M KCl containing 5.0 mM $Ru(NH_3)_6Cl_3$. Limiting current at –0.4 V vs. SCE is shown to be independent of rotation velocity; limiting current at –0.75 V vs. SCE is shown (inset) to be linear with (rotation velocity)$^{1/2}$. Coverage of $(PQ^{2+})_n$ was determined by slow sweep (10 mV/s) cyclic voltammetry (-·-·) in aqueous 1.0 M KCl.

It has proven useful to examine the mediated reduction of $Ru(NH_3)_6^{3+}$ at Au, Pt, and W electrodes functionalized with I. Using rotating disk Pt(naked) electrodes we observe mass transport limited current for the reduction of 5 mM $Ru(NH_3)_6^{3+}$ at electrode potentials ($\sim$–0.4 V) that would be expected based on the E° for the couple (Figure 9). This conclusion follows from linear plots of reduction current at –0.5 V vs. SCE against (rotation velocity)$^{1/2}$ for our fast rotation rates, $\sim$2000 rpm. However, at electrodes functionalized with I ($\sim 10^{-8}$ mol of PQ^{2+}/cm^2) the reduction is effectively blocked, and only when the $(PQ^{2+})_n$ is reduced to $(PQ^{+\cdot})_n$ (more negative than $\sim$–0.6 V vs. SCE) is a mass transport limited current observed for the reduction of the 5 mM $Ru(NH_3)_6^{3+}$ (Figure 9). Generally, there is some cathodic current at potentials where $Ru(NH_3)_6^{3+}$ reduction occurs on the naked electrodes, but in some cases <2% and in most cases <15% of the cathodic current observed at the naked electrode at –0.3 V is observed for the electrodes functionalized with I. Further, the small amount of current that does occur at the usual potential would appear to be due to diffusion of $Ru(NH_3)_6^{3+}$ through the $(PQ^{2+})_n$ layer, since the current is nearly independent of rotation velocity. Incorporation of Pt(0) into the $(PQ^{2+})_n$ layer does not affect the ratio of current at –0.6 V vs. SCE to that at –0.3 V vs. SCE. This result shows that the usual $[(PQ^{2+})_n\cdot nPt(0)]_{surf.}$

Scheme VII. Representation of the Ideal Result from Direct Platinization of a p-Type Semiconductor (left) and from Dispersion of Pt(0) into a Redox-Active Polymer Derived from Reagent I (Right)



polymer is not an electronic conductor. This follows from the fact that the mechanism of $Ru(NH_3)_6^{3+}$ reduction by the electrodes derivatized with I must be that represented by eq 7. If the $[(PQ^{2+})_n{\cdot}nPt(0)]_{surf.}$ system were an electronic conductor, the current–voltage characteristic would approach that for the naked electrodes; reduction would need not involve a prior reduction of the $(PQ^{2+})_{surf.}$. Apparently, the amount of Pt(0) bound in $(PQ^{2+})_n$ is not sufficiently great to bring about significant electronic conductivity.

The shapes of the current–voltage curves in Figure 9 for the rotating disk electrode deserve comment. In particular, note the presence of a peak at ~−0.6 V vs. SCE for the electrode bearing $(PQ^{2+})_n$. This peak corresponds to the reduction of $(PQ^{2+})_n$ to $(PQ^{+\cdot})_n$; this peak declines with scan rate diminution and is essentially unobserved at a scan rate of 2 mV/s.

The experiments with $Ru(NH_3)_6^{3+}$ reduction at the electrodes derivatized with I show that (i) k_{et} in eq 7 is large enough to accommodate a mass transport limited current at 10 mM $Ru(NH_3)_6^{3+}$ and (ii) the electrodes are typically fully covered with $(PQ^{2+})_n$, though $Ru(NH_3)_6^{3+}$ can diffuse through to the underlying surface to be reduced. The value of k_{et} is expected to be large,[33] since the driving force for reaction is large (~0.3 V) and the self-exchange rates of the two electron-transfer partners are sufficiently large.[34,35] The $(PQ^{2+})_n$ polymer undergoes redox reaction sufficiently fast that >15 mA/cm² current density for reduction of $Ru(NH_3)_6^{3+}$ according to eq 7 can be observed. The current for $Ru(NH_3)_6^{3+}$ reduction by the surface $(PQ^{+\cdot})_n$ is the same when Pt(0) has been introduced. Thus, referring to Scheme VI, the current density through the polymer overlayer can exceed 15 mA/cm².

The slow rate of $Ru(NH_3)_6^{3+}$ reduction via the diffusion into the polymer could be due to several factors. First, the diffusion in and out is likely to be very slow compared to that for $Ru(NH_3)_6^{3+}$ in the bulk. Second, the steady-state amount of $Ru(NH_3)_6^{3+/2+}$ in the polymer is likely to be low, and the rate of mediated reduction of $Ru(NH_3)_6^{3+}$ via the $Ru(NH_3)_6^{3+/2+}$ in the polymer may be limited by the rate of electron transfer (self-exchange) among the $Ru(NH_3)_6^{3+/2+}$ in the polymer. And third, the self-exchange rate of the $Ru(NH_3)_6^{3+}$ is not so large that mass transport limited current could be observed for the mediation by the polymer-bound $Ru(NH_3)_6^{3+/2+}$. It is noteworthy that the $Ru(NH_3)_6^{3+}$ is found at all in the polymer layer, since the polymer monomers bear a 2+ charge and the $Ru(NH_3)_6^{3+}$ a 3+ charge. However, the concentration of the $Ru(NH_3)_6^{3+}$ in the polymer is likely much less than in the bulk solution.

Since $Ru(NH_3)_6^{3+}$ can diffuse through the $(PQ^{2+})_n$ layer to be reduced, it is perfectly reasonable that H_2 evolution can occur at the M/polymer interface particularly in the case of M = Pt. Indeed, the Pt/$(PQ^{2+})_n$ without Pt incorporated into the polymer reveals that the $(PQ^{+\cdot})_n$ can effect H_2O reduction by way of the underlying Pt surface. This is established by holding the derivatized Pt electrode at −0.6 V vs. SCE until the $(PQ^{2+})_n$ is completely reduced to the observably purple $(PQ^{+\cdot})_n$ under Ar. The electrode is then taken out of potentiostatic control and allowed to equilibrate with the aqueous electrolyte solutions. At pH 1.1 the equilibration to regenerate $(PQ^{2+})_n$ is virtually instantaneous, while at pH 8.6, where $(PQ^{+\cdot})_n$ is incapable of reducing H_2O, the $(PQ^{+\cdot})_n$ remains in the reduced state indefinitely.

To summarize results from the study of Au, Pt, W, and n-MoS_2 electrodes modified with the $(PQ^{2+})_n$ and $[(PQ^{2+})_n{\cdot}nPt(0)]_{surf.}$ systems, we observe that (i) the coverage of the polymer is sufficiently uniform that normally reversible couples can be blocked by the polymer, but in some cases redox active species can diffuse through the polymer; (ii) the Pt(0) incorporated into $(PQ^{2+})_n$ does not alter the response to $Ru(NH_3)_6^{3+/2+}$, showing that $[(PQ^{2+})_n{\cdot}nPt(0)]_{surf.}$ is not an electronic conductor; (iii) a steady-state current of >15 mA/cm² can pass through the $(PQ^{2+})_n$ overlayer; (iv) the Pt(0) in $[(PQ^{2+})_n{\cdot}nPt(0)]_{surf.}$ is dispersed through the polymer determined by Auger spectroscopy; and (v) the $(PQ^{+\cdot})_n$ mediates H_2 reduction on Pt electrodes. These results support the conclusion that the $[(PQ^{2+})_n{\cdot}nPt(0)]_{surf.}$ yields improvement in H_2 evolution kinetics by the mechanism represented in Scheme VI for illuminated p-type Si: first reduction of $(PQ^{2+})_n$ and then equilibration with the dispersed Pt(0) to reduce H_2O to H_2. Results for n-type MoS_2, which is not efficiently platinized by mere dipping into $PtCl_6^{2-}$ solution, directly support the conclusion that the dispersed Pt(0) provides a good current density for H_2 evolution.

Discussion

Scheme VII idealizes the two types of modified photocathodes that we have investigated. The results establish that either direct platinization or functionalization with a redox polymer from I followed by dispersion of Pt(0) into the polymer gives a significant improvement in the efficiency for the photoelectrochemical generation of H_2. However, neither the platinized surfaces nor the surfaces bearing $[(PQ^{2+})_n{\cdot}nPt(0)]_{surf.}$ behave in the manner expected from the ideal representations in Scheme VII. For the platinized surface no pH dependence on efficiency of photoelectrochemical generation of H_2 is expected for the current densities that we have examined, since a p-Si/SiO_x/Pt interface would not be affected if only Pt contacts the aqueous electrolyte. But by the procedure that we use to achieve optimum efficiency, the

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(33) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679. (c) Lewis, N. S.; Bocarsly, A. B.; Wrighton, M. S. *J. Phys. Chem.* **1980**, *84*, 2033.

(34) Meyer, T. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 2369.

(35) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.

modified surface that results does yield a pH-dependent efficiency. The data are most consistent with a p-Si/SiO_x/Pt interface where the interface energetics are dominated by the contact of the aqueous solution with essentially exposed p-Si/SiO_x (Scheme III). An important role for the SiO_x layer is implied from studies showing that sputtering Pt onto clean p-Si results in a p-Si/Pt interface giving only a small amount of band bending.[36] For Si/liquid electrolyte interfaces it has already been pointed out that SiO_x plays an important role in establishing the interface energetics.[7,25,37]

The photoelectrodes bearing the $[(PQ^{2+})_n \cdot nPt(0)]_{surf.}$ do give an efficiency vs. pH profile for H_2 generation that is expected for a mechanism involving prior reduction of $(PQ^{2+})_n$. However, the decline in efficiency for mediated H_2 evolution at high pH's is not as sharp as would be expected for mediation only via $(PQ^{+\cdot})_n$. Higher than expected efficiency at high pH is possibly due to a small amount of Pt(0) that does contact the p-Si/SiO_x. The amount of Pt(0) at the interface is too small, though, to account for a significant current density. The alternative explanation for high efficiency at high pH is that the $(PQ^0)_n$ becomes important as a mediator at sufficiently negative potentials. For the p-Si electrodes functionalized with I, depth profile analysis shows that there is a thin SiO_x layer between the bulk Si and the $(PQ^{2+})_n$ polymer.[7] Again, this oxide layer likely plays an important role in determining the photovoltaic properties of the interface.

While neither of the two surface modifications yield truly durable photoelectrochemical systems, the results do show that surface modification is a viable approach to solving the problem of sluggish H_2 evolution kinetics. Of all of the p-type semiconducting photocathodes examined, only p-type $LuRhO_3$[38] has been claimed to have inherently good H_2 evolution kinetics.[1-7] Thus, approaches to improving kinetics are needed. Previously,[1-6] we and others have shown that reagents like MV^{2+} are relatively (relative to H_2O) efficiently reduced at illuminated p-type semiconductor photocathodes. Such results establish that it is possible to photoelectrochemically produce reductants capable of reducing H_2O. In fact, the remote catalysis of the process represented by eq 9 is a way to avoid the problem of dispersed H_2 generation in

$$2A + 2H_2O \xrightarrow[\text{catalyst}]{\Delta} 2A^+ + 2OH^- + H_2 \qquad (9)$$

solar energy conversion schemes. Such systems would require finding a catalyst for the equilibration of the (A^+/A) couple with (H_2O/H_2); thus far Pt has been the catalyst chosen for $A = MV^{+\cdot}$, for example.[32,39] It is noteworthy that the use of $(MV^{2+/+\cdot})$ in solution as an electron relay system for H_2 evolution gives the same sort of pH vs. efficiency profile[40] as we find for the surface-confined polymer derived from I. For $A = MV^{+\cdot}$, Pt is not necessarily a good practical choice for the catalyst since the Pt catalyzes the hydrogenation of $MV^{+\cdot}$ to the fully saturated organic compound.[32] The photoelectrochemical generation of A followed by remote catalysis as in (9) is a practical option in competition with surface modifications.

Unless there is an effect on the interface energetics that influences the maximum value of E_V there is no fundamental reason why one procedure for improving H_2 evolution is superior to another in terms of efficiency. That is, unless the Si/SiO_x is altered there is no basis for a change in ideal efficiency from one catalyst to another. However, there are reasons why one system might be superior to another in practical terms. For example, it might be desirable to run the photoelectrolysis at a particular pH in order to have optimum efficiency at the anode. The directly platinized surface has the smaller pH dependence and would seem to offer an advantage in this regard. On the other hand, modification of the redox polymer in the polymer/Pt(0) system could be done easily to change $E^{\circ\prime}$ so that an optimum pH higher or lower than 4 could be obtained. Other advantages and disadvantages will be described in the paragraphs below.

The uniform coverage of $(PQ^{2+})_n$ that is possible may allow a higher current density than when the Pt(0) is directly applied. The point is that the polymer is a pure, fast electron acceptor while the direct platinization yields non-uniform coverage. However, the non-uniform Pt(0) coverage does not seem to be a difficulty in achieving a current density similar to or even exceeding that from the $[(PQ^{2+})_n \cdot nPt(0)]_{surf.}$ system. Indeed, at some current density the polymer is likely to be limited by ion (or charge) transport through the polymer, while no similar limitation exists for the electronic conducting Pt(0).

A second possible advantage for the $[(PQ^{2+})_n \cdot nPt(0)]_{surf.}$ is that smaller amounts of Pt(0) can be used for longer periods of time. The durability of the Pt(0) in the polymer may be improved if the Pt(0) does not aggregate. The results so far indicate that neither platinization nor the polymer/Pt(0) system yields a durable interface. Similar amounts of Pt(0) have been used in each case. Perhaps surprisingly we do not find that the $(PQ^{2+})_n$ is hydrogenated as is the case when the $(MV^{2+/+\cdot})$ is catalyzed to give H_2 where colloidal Pt is used as the catalyst.[32] The rationale for the lack of significant hydrogenation is that the polymer is relatively rigid and the aromatic rings may not be able to come close enough to the Pt surfaces. Equilibration of the $(PQ^{2+/+\cdot})_n$ with Pt is likely by an outer-sphere mechanism involving no intimate interaction of the $(PQ^{2+/+\cdot})_n$ with the Pt_y/Pt_yH_x. The lack of durability of the polymer/Pt(0) system seems to be associated with the loss of activity of the Pt(0). This may reflect the fact that more extensive aggregation occurs with time. The hope is that a redox polymer will matrix isolate very active, small Pt aggregates to allow sustained, efficient catalysis of H_2 evolution. But for now, we cannot claim complete success in this regard.

Another factor that could contribute to lack of durability of the polymer/Pt(0) system and not of the Pt(0) alone system is the mechanical disruption caused by H_2 gas evolution. This suggests that the catalyst for H_2 evolution might be best located at the polymer/liquid interface. Our synthetic efforts are now directed toward this end. It is also possible that the dispersion of the catalyst contributes to lower efficiency, since the dispersion of the Pt(0) into the $(PQ^{2+})_n$ seems to lower E_V with respect to the $E^{\circ\prime}(PQ^{2+/+\cdot})_n$.

Both the $(PQ^{2+/+\cdot})_n$ and Pt(0) are light absorbers in the visible region of the spectrum. At this point, we do not regard light absorption by the surface modifiers to be a significant detractor from attaining high efficiency, since the quantum yields for electron flow are quite good (Tables I and III), at the highest efficiency. Practical systems, though, may require the use of more transparent systems, especially for the polymer that might undergo photodegradation.

Turnover number and turnover rate for the surface redox polymer system are important parameters. For example, 20 years of constant output in a solar application at ~ 25 mA/cm^2 for an 8-h day would require $> 10^9$ $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$ cycles for a coverage of PQ^{2+} of $\sim 10^{-8}$ mol/cm^2. This staggering turnover number may yet be attainable, since studies of electrochromic displays based on redox cycling of *N,N′*-dialkyl-4,4′-bipyridinium reagents are quite promising.[41] For the reasons mentioned above, the turnover numbers may be lower when Pt(0) is incorporated (hydrogenation) and when H_2 gas is liberated (mechanical disruption), but it is likely that redox reversibility of polymers could be good enough. Turnover rate at a coverage of 10^{-8} mol/cm^2 must be 25 s^{-1} per PQ^{2+} to achieve 25 mA/cm^2. We have demonstrated > 15 mA/cm^2 and believe that 25 mA/cm^2 is achievable. Even platinized Pt has an overvoltage[42] of ~ 40 mV at ~ 25

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mA/cm^2, so we can expect a small loss in efficiency if for no other reason than this as current density approaches such high values.

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Reactivity of $[\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)](\eta\text{-}C_5H_5)_3Ti_2$ with Dinitrogen. Structure of a Titanium Complex with a Triply-Coordinated N_2 Ligand

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Abstract: The titanium metallocene complex, μ-(η^1:η^5-cyclopentadienyl)-tris(η-cyclopentadienyl)dititanium(*Ti-Ti*), $[\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)](\eta\text{-}C_5H_5)_3Ti_2$ (**1**), displays a wide range of chemical reactivity with dinitrogen. In hydrocarbon solvents **1** reacts reversibly with N_2 to yield a deep blue complex of composition $[(C_5H_4)(C_5H_5)_3Ti_2]_2N_2$. Reaction of **1** with N_2 ($\sim$10 atm) in 1,2-dimethoxyethane (glyme) yields N_2 complex **3** characterized by ν(N–N) = 1222 cm^{-1}, the lowest N–N vibrational frequency yet observed for any coordinated dinitrogen ligand. Reaction of **3** with tetrahydrofuran (THF) yields N_2-complex **4** with ν(N–N) = 1296 cm^{-1}. Successive treatment and workup of **3** with THF/glyme and bis(2-methoxyethyl) ether (diglyme) gave a crystalline N_2 complex **5** with ν(N–N) = 1282 cm^{-1}. The composition and structure of **5** was determined by single-crystal X-ray crystallography as $(\mu_3\text{-}N_2)[(\eta^5{:}\eta^5\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2Ti_2][(\eta^1{:}\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3Ti_2]\cdot[(\eta\text{-}C_5H_5)_2(C_6H_{14}O_3)Ti]\cdot C_6H_{14}O_3$ (**5**). In this complex, the dinitrogen ligand is coordinated simultaneously to three titanium atoms. The N_2 is σ bonded to the one formally divalent titanium atom in $[\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)](\eta\text{-}C_5H_5)_3Ti_2$. It is also coordinated in what may be described as a σ,π mode to the two titanium atoms in $(\eta^5{:}\eta^5\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2Ti_2$. As a result of the multiple coordination, the N–N length [1.301 (12) Å] in **5** is considerably longer than in free dinitrogen [1.0976 Å], and is intermediate between that for azo (–N=N–) and hydrazo (>N–N<) compounds. Treatment of solutions of **5** with H_2 gas, or with dry HCl, results in a loss of most of the coordinated dinitrogen (as N_2). However, aqueous hydrolysis of **5** in diglyme yields mostly ammonia. The implications of this chemistry to N_2-fixation systems are discussed.

Low-valent bis(η-cyclopentadienyl)titanium complexes[1b,c] have been widely employed as reagents and catalysts in chemical reactions with small unsaturated molecules, e.g., hydrogen and olefins,[2,3] acetylene,[4] carbon dioxide,[5] carbon monoxide,[6] ammonia,[7] and nitrogen oxides.[8] However, their most striking property is the often extraordinarily facile reactivity with dinitrogen.

It was shown in 1964 by Vol'pin, Shur, and co-workers[9] that mixtures of bis(η-cyclopentadienyl)titanium dichloride and Grignard reagents could stoichiometrically reduce dinitrogen to ammonia. The specific organometallic titanium species responsible for this N_2 reduction has not been identified.[10,11] However, the proposed coordination of dinitrogen to titanium has since been demonstrated by the isolation of several titanium N_2 complexes such as μ-dinitrogen-tetrakis(η-pentamethylcyclopentadienyl)-dititanium, $[(\eta\text{-}C_5[CH_3]_5)_2Ti]_2N_2$,[12] and μ-dinitrogen-bis(p-tolyl)tetrakis(η-cyclopentadienyl)dititanium, $[(\eta\text{-}C_5H_5)_2(p\text{-}C_6H_4CH_3)Ti]_2N_2$.[13] These have been isolated as discrete, crystalline solids and their structural and chemical properties carefully investigated. Deep blue dinitrogen complexes of stated composition $[(C_5H_5)_2TiR]N_2$ (R = alkyl),[14] $[(C_5H_5)_2Ti]_{1-2}N_2$,[15] and $[(C_5H_5)_2Ti]_2N_2$[16] have been reported and are widely referred to in the literature. Unfortunately, these complexes were not well characterized and their stated composition and structure are, at best, doubtful. Interesting titanium dinitrogen complexes, displaying unusually low ν(N–N) vibrational stretching frequencies, have been described by Borod'ko, Shilov, and co-workers.[17,18] The

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